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QUALITY ASSURANCE/ QUALITY CONTROL PERFORMANCE REPORT

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QUALITY ASSURANCE/QUALITY CONTROL PERFORMANCE REPORT

WATER ANALYSIS AND RESEARCH BRANCH

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FOREWORD

The Quality Assurance/Quality Control (QA/QC) Performance Report was initiated to provide a comprehensive information base that describes the routine analytical performance characteristics for a majority of the analytical determinations completed in the Water Analysis and Research Laboratory during the staged implementation of the complete QC program. The data is presented in genuine, unbiased statements of the observed analytical performance of each methodology.

The comprehensive QA/QC program consists of a complementary set of analytical tasks completed on a daily, monthly, quarterly, and yearly basis. The following functions describe the routine QA/QC procedures for most of the analytical systems operated in the Water Analysis Laboratory.

Analysis of Standards
Analysis of QC Solutions QCA, QCB, and QCBlank
Analysis of Recovery Solutions
Analysis of Randomly Selected Duplicates
Analysis of Within-run Sensitivity Checks
Analysis of Standard Reference Materials
Analysis of Blind Duplicates
Participation in Internal & External Collaborative Studies
Comprehensive Calibration Check
Participation in QC Studies of Support Apparatus

Each of the above integral parts of the QA/QC program will be described in the Quality Control Procedures of the Introduction Section of this report.

During September and October of 1981, the principles associated with Youden's two sample technique and applications of a formal quality control program based upon QCA, QCB and QCBLANK (1) were introduced to staff of the Water Analysis Laboratory. The implementation of the program was staged to permit analysts to become familiar with the proposed program and prepare the

necessary solutions to be analyzed. Due to the variety of determinations performed by the Branch and the requirements of the QA/QC programs, many test methodologies need specialized QC materials which have been recently developed or are currently under development.

This report is intended to be the first in a series of reports that will enable the users of the analytical data to assess the performance characteristics including the accuracy and precision of the analytical systems during a specified time frame.

In addition to the normal delays in collecting and processing the data, considerable effort had been invested in the adoption of a singular and concise format that will enable the user to select pertinent information from the report series. Recommendations to modify the existing format or include additional laboratory information would be considered helpful.

ACKNOWLEDGEMENTS

The data produced, collected, and summarized in this report required the participation and involvement of all technical and supervisory staff in the Water Analysis and Research Branch. The basis for the QA/QC program is derived from Youden's two sample evaluation approach for the interpretation of intercomparison results (1) and King's extension of the Youden application to establish a routine quality control program (2).

The continuing efforts of Mr. L. Goodwin in coordinating quality control studies in the Water Analysis Laboratory is gratefully acknowledged. The typing of draft manuscripts by Mrs. Susan Stecyk and Mrs. Connie Baxandall of the Chemistry Division is greatly appreciated.

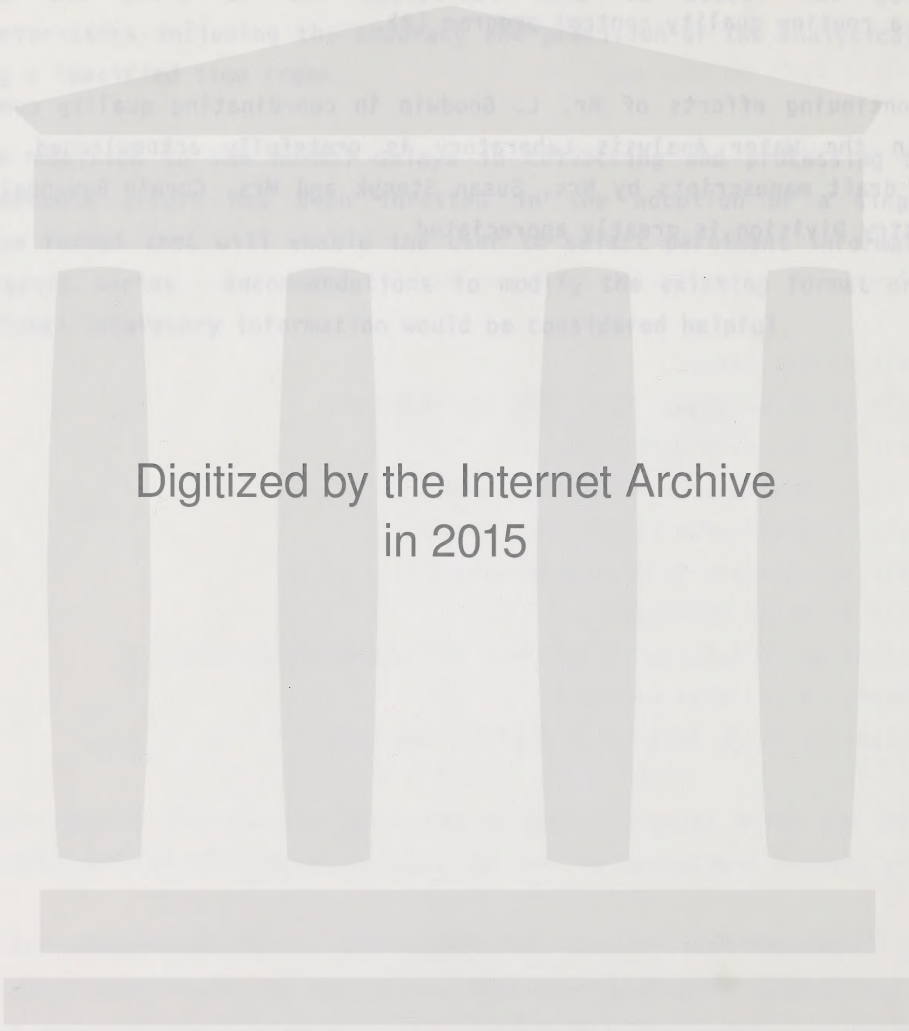

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TABLE OF CONTENTS

PAGE

FOREWORD..... i
ACKNOWLEDGEMENTS..... iii
LIST OF TABLES..... vi
INTRODUCTION..... 1
INTERPRETATION OF THE PERFORMANCE REPORT..... 2
QUALITY ASSURANCE PROCEDURES..... 6
Analysis of Standards..... 6
Analysis of QC Solutions..... 6
Analysis of Recovery Solutions..... 8
Analysis of Randomly Selected Duplicates..... 8
Analysis of Within-run Sensitivity Checks..... 10
Analysis of Standard Reference Materials..... 10
Analysis of Blind Duplicates..... 11
Participation In Internal and External Collaborative Studies..... 11
Comprehensive Calibration Check..... 12
QA/QC Studies of Support Apparatus..... 12
The A, B Quality Control Technique..... 13
QUALITY CONTROL DATA..... 16
ALKALINITY, Total..... 17
ALUMINUM, Extractable..... 19
ARSENIC, Total..... 21
BARIUM, Total..... 23
BERYLLIUM, Total..... 25
BORON, Filtered..... 27
CADMIUM, Total..... 29
CALCIUM, Filtered..... 31
CARBON, INORGANIC, Dissolved..... 33
CARBON, ORGANIC Dissolved..... 35
CARBON, Particulate..... 37
CHLORIDE, Filtered..... 39
CHROMIUM, Total..... 41
COBALT, Total..... 43

TABLE OF CONTENTS CONTINUED

PAGE

COPPER, Total..... 45
CYANIDE, Simple Extractable..... 47
FLUORIDE, Filtered..... 49
IRON, Acid Extractable..... 51
LEAD, Extractable..... 53
MAGNESIUM, Acid Extractable..... 55
MANGANESE, Total..... 57
MERCURY, Total..... 59
MOLYBDENUM, Total..... 61
NICKEL, Total..... 63
NITROGEN-AMMONIA, Dissolved (LOW RANGE)..... 65
NITROGEN-AMMONIA, Dissolved (HIGH RANGE)..... 67
NITROGEN-KJELDAHL, Total..... 69
NITROGEN-NITRATE+NITRITE, Filtered (Low Range)..... 71
NITROGEN-NITRATE+NITRITE, Filtered (High Range)..... 73
NITROGEN-NITRITE, Filtered (Low Range)..... 75
NITROGEN-NITRITE, Filtered (High Range)..... 77
NITROGEN, Particulate..... 79
OIL & GREASE..... 81
OXYGEN DEMAND, Biochemical..... 83
OXYGEN DEMAND, Chemical..... 85
pH..... 87
PHENOLIC COMPOUNDS..... 89
PHOSPHORUS, Filtered Reactive..... 91
PHOSPHORUS, Total..... 93
POTASSIUM, Filtered..... 95
SELENIUM, Total..... 97
SILICA, Filtered Reactive..... 99
SODIUM, Filtered..... 101
SOLIDS, Total..... 103
SOLIDS, TOTAL SUSPENDED..... 104
SPECIFIC CONDUCTANCE..... 105

TABLE OF CONTENTS CONTINUED

PAGE

SULPHATE, Filtered..... 107
SURFACTANTS (Methylene Blue Active Substances)..... 109
TANNIN AND LIGNINS..... 111
TURBIDITY..... 113
VANADIUM, Total..... 115
ZINC, Total..... 117
DISCUSSION..... 120
RECOMMENDATIONS..... 128
REFERENCES..... 129

LIST OF TABLES

PAGE

Table 1. Useful Linear Range for Non-Linear Analytical Systems.. 120

Table 2. Comparison Between Precision Data Obtained from Duplicate Analysis with Within-Run and Between-Run Standard Deviation Calculated from QCA and QCB Data.... 122

Table 3. Comparison of Detection Limits Using Duplicate Data Method with the Instrumental Detection Limits (1987)... 125

INTRODUCTION

INTRODUCTION

During the cumulative processes associated with obtaining analytical data, numerous factors must be considered when judging the reliability of the results. The most important factors that affect the meaningfulness of analytical results include the following.

1. Sampling and sample-related factors constitute a foundation for all subsequent analytical work and generally provide the significant factor(s) in validating analytical data. Since the sampling event is external to the responsibilities of the analytical laboratory, its contribution to the overall variance cannot presently be identified accurately by analysis of single samples sent to the laboratory. In the process of determining the variance in the analytical data which is directly or indirectly attributed to the sampling process, the use of field replicates, blanks, and standards cannot be overemphasized.

2. Analytical methodologies are frequently chosen by laboratory staff on the basis of the number and classification of samples to be analyzed and the most frequent concentration range characteristics for the majority of the samples. The requirements of mutually agreeable special project work, operating funds, and capital funds associated with the laboratory's operational budget are also key factors in selecting appropriate methodologies to produce analytical data.

3. Performance data document calibration stability as well as within-run and between-run reproducibility under controlled conditions. Precision data are based upon the use of random samples analyzed in duplicate. Accuracy is determined from the analysis of reference materials of known concentrations as well as of spiked samples. Improving the skills of the analyst and increasing the scientific support provided by professional staff will provide constructive evaluation of existing methodologies and analytical capabilities, and improvements in the statistical handling of analytical data.

INTERPRETATION OF THE PERFORMANCE REPORT

Within the context of this performance report, a number of analytical laboratory and statistical terms are defined to ensure consistent interpretation of the QA/QC data.

Deviation: Unavoidable, small random fluctuations inherent to the normal measurement process.

Error: The numerical difference between a measured value and the true value.

Systematic Errors: The result of factors which cause the analytical signal to be biased high or low from the correct value, often by a fixed amount or a fixed fraction. The effect of a systematic error can be predicted a priori and if the cause is known, it can be eliminated or compensated for. Such errors can be due to numerous causes and are often divided into interference or matrix errors, calibration errors, instrumental or measurement errors, sample preparation errors, or sample acquisition errors.

Random Errors: Errors indeterminate in magnitude and sign, and whose appearance does not conform to any apparent laws. They arise in every measurement, which includes any analytical determination. They are revealed by the fact that repeated determinations of a particular parameter in a sample, carried out by the same method generally give results which are not absolutely identical.

Precision: Refers to the reproducibility among replicate determinations. In an analytical QA/QC program, precision is determined, not on reference standards, but by the analysis of actual water samples which cover a range of concentrations and a variety of interfering materials usually encountered by the analyst.

Accuracy: Refers to the agreement between the amount of a component measured by the test method and the amount actually present.

Standard Deviation: Measures the reproducibility of analytical measurements of a sample analyzed in replicate. It can be determined in one of two experimental approaches.

1. If a single sample is analyzed n times, the standard deviation s, which may be thought of as a root mean square deviation of values from their average X, is calculated using the formula:

$$s = \left(\sum_{i=1}^{i=n} (X_i - \bar{X})^2 / (n - 1)\right)^{0.5}$$

2. If n samples are analyzed each in duplicate, X_1 and X_2, the standard deviation is calculated using the formula:

$$s = \left(\sum_{i=1}^{i=n} (X_1 - X_2)^2 / 2n\right)^{0.5}$$

where n is the number of duplicate sets and $(X_1 - X_2)$ is the difference of duplicate measurements.

The standard deviation based upon replicate analysis of a single sample presents an optimistic estimate of precision at this particular sample concentration. However, the standard deviation based upon samples of different concentration analyzed in duplicate enables the user to identify the variation of precision with analyte concentration. In this report duplicate data, for each

parameter, were grouped into three concentration ranges, 0 to 20%, 20 to 50%, and 50 to 100% of full scale, and the precision at each range was then evaluated. According to the theory of errors it can be asserted that about 68.26% of all the values fall within the limits $X \pm s$, while $X \pm 2s$ includes about 95% and $X \pm 3s$ includes practically all (99.74%) the values.

Within-run Standard Deviation: A statement of the expected range of deviations obtained from a continuous measuring system in which the calibration remains unchanged. This estimate is useful to the user of data when attempting to rationalize differences in data obtained where samples are analyzed within a single analytical run. It is calculated using the equation:

$$s_w = (s_D^2/2)^{0.5}$$

where s_D^2 is the variance of the difference between QCA and QCB data.

Between-run Standard Deviation: A statement of the expected range of deviations obtained from a measuring system operated under different calibration conditions. This estimate is useful to the user of the data when attempting to rationalize differences in data obtained from separate samplings which are likely analyzed in two distinct analytical runs. It is calculated using the equation:

$$s_b = ((s_A^2 + s_B^2)/2)^{0.5}$$

where s_A^2 and s_B^2 are the variances of QCA and QCB data, respectively.

Detection Limit: The detection limit (D.L.) of an analytical system is regarded as being the lowest concentration of the analyte that can be distinguished with high confidence from a field blank, here defined as a hypothetical sample containing zero concentration of analyte. In many instances, a realistic field blank may not be available. The detection limit is estimated from the standard deviation (s) of duplicate data falling in the concentration range of 0-20% of full scale. The detection limit is given by:

$$D.L. = K \times s$$

A value of K = 3, based upon the 99.9% confidence level, is "strongly recommended" by the International Union of Pure and Applied Chemistry (IUPAC) (3).

QUALITY ASSURANCE PROCEDURES

The quality assurance (QA) program adopted by the Water Analysis Laboratory consists of a group of at least 10 integrated procedures previously identified in the Foreword Section of this report. Each procedure will be described in detail and the interaction between the procedures will be revealed.

Analysis of Standards. After the analytical system has been stabilized, a series of standards is analyzed to establish a calibration curve which provides a concentration-instrument response statement for the analytical system on a daily-run basis. The series of standards may be as few as one (e.g. ICP) or as many as ten (e.g. $SO_4^{=}$) depending upon the calibration stability of the analytical system as well as the calibration function of the system (i.e. linear or nonlinear). Calibration curves for automated colorimetric systems are frequently reproducible within a very small envelope of uncertainty. Significant changes in slope or blank are not likely to occur and deviation from historical performance is usually a result of improper preparation of standards or one or more of the reagents.

Analysis of QC Solutions. Quality control solutions (QCA, QCB, QCB1) are prepared from independent reference materials that are separate and distinct from materials utilized to prepare standards. A frequent misunderstanding exists between the purpose and utilization of standards versus quality control solutions. Standards, which are usually prepared on the day they are used, are utilized to prepare an instrument response-concentration curve, i.e. a calibration curve. Quality control solutions are utilized to confirm an accurate calibration curve within specified calculated limits. A majority of the analytical systems routinely operated in the Water Analysis Laboratory have a well-defined history of instrument response-concentration calibration curve which is usually determined for each analytical run using a series of 1 to 5 standards.

The concentrations of QCA and QCB are chosen to be different from the standards utilized to calibrate the system. QCB1, (a pure solvent or digestion blank level), is prepared from the diluent water used to prepare QCA and QCB. The concentrations of the quality control solutions are chosen such that QCA and QCB usually provide an instrument response of 75% and 25% of full scale, respectively. Other concentration combinations for QCA and QCB are possible e.g. two low concentrations or two high concentrations, depending upon the performance and the normal operating characteristics of the analytical system. QCA, QCB, and QCB1 are prepared in sufficient volume to provide at least 20 days of analysis. Analysis of old and new QC solutions must overlap for at least three days before new QC solutions are adopted to control and verify the analytical system. During the Comprehensive Calibration Check, the QC solutions are verified by the analysis of standard reference materials.

Analysis of Recovery Solutions. Recovery solutions are used to measure the conversion of one chemical species to another usually for the purpose of analysis by a specific methodology. Examples of routinely analyzed recovery solutions include:

1. determining the efficiency of an oxidation/reduction procedure such as the conversion of nitrate to nitrite using a cadmium column;
2. determining the completeness of a digestion procedure by the analysis of recovery reagents for TKN and TP analysis; and
3. determining the recovery of glucose-glutamic acid and the seed correction for BOD analysis.

Digestion blanks and seed corrections in single, double or multiple doses are necessary to estimate an accurate daily blank level. Analysis of recovery solutions as paired duplicates confirm the reproducibility of the entire digestion process and an accurate digestion blank. The reference materials for recovery check solutions are selected to provide a nil response (ideal) if a pretreatment process is not completed according to the established analytical methodology. Often a complete (100%) recovery is not a requirement; however reproducible recoveries are essential.

Analysis of Randomly Selected Duplicates. The first three samples of each analytical run consist of three randomly selected samples from the daily worklist. Independent aliquots of the same samples are reanalyzed in the normal numerical sequence in the tray pattern.

The analysis of duplicate sample data provides a mechanism of measuring in-run analytical performance for an analytical procedure. Although the duplicates are not 'blinds' to the analyst, the random distribution of the replicates throughout the run should provide a reasonable, unbiased estimate of repeatability under routine conditions. The accumulated duplicate data document the following information.

1. The distribution of difference between duplicates throughout the operating range.
2. The distribution of numbers of samples versus concentration range to evaluate the suitability of the operating range.

3. The within-run standard deviation for the analytical process for selected levels of concentration under routine conditions.
4. A review of duplicate data by the analyst at the end of the analytical run and a comparison of the day's precision with the historical record.
5. An estimate of the detection limit of the analytical system using the standard deviation within the 0 to 20% range of full-scale.

Dr. M. Habib extended D. King's manual dot diagram for calculating standard deviation to a simple computer model that allows the analyst to instantly monitor the level of reproducibility of the analytical system and make appropriate decisions about the performance of the system when necessary. The method outlined below describes the steps involved to evaluate the between-run precision at different concentration ranges of the routine samples analyzed.

1. The analytical range of the method is divided into three concentration ranges varying from 0 to 20%, 20 to 50%, and 50 to 100% of full scale.
2. Duplicate data are sorted out and then entered into their appropriate ranges.
3. The standard deviation, s, is calculated for each duplicate set.
4. The precision, defined as % Relative Standard Deviation (% RSD), is calculated using the formula

$$\% \text{ RSD} = \frac{s}{x} \times 100$$

Where x is the average of the duplicate set x_1 and x_2. When sufficient data have been accumulated in this fashion, the number of duplicate sets, n, within each range is counted and the average standard deviation, s, and the average precision % RSD are then calculated using the formulas.

$$\bar{s} = \frac{s}{n}$$

and

$$\% \overline{\text{RSD}} = \frac{\% \text{ RSD}}{n}$$

Analysis of Within-run Sensitivity Checks. Sensitivity changes within an analytical run of samples are monitored using a low level standard (L=10% of full-scale) and a high level standard (H=80% of full-scale) which were previously analyzed during the preparation of the calibration curve. The washwater blank is also analyzed to establish a uniform estimate of the baseline position. In all automated analytical systems, a uniform tray pattern has been established to ensure comprehensive evaluation and correction for sensitivity changes and baseline drift which result from chemical and physical influences on the analytical system. The traditional tray pattern after calibration, QC confirmation, and analysis of random duplicates consists of:

Bl, 10 samples, L, H, Bl, 10 samples, Bl, 10 samples, L, H, Bl,...

The baseline is established from the previous washwater blank to the next washwater blank. Random sample cup contamination effects are determined from washwater blanks and low level sensitivity checks. Before any correction of the raw data occurs, changes in sensitivity are confirmed by the analytical results for the high and the low level sensitivity check standards. The decision to repeat an analytical run of samples due to random contamination effects or to correct analytical results because of sensitivity changes is always based upon the corroborated evidence of multiple observations for two or more test solutions. The entire run of samples should be repeated when sensitivity changes exceed 10% of normal values. Correction factors must be clearly identified on the bench sheet of analytical data.

Analysis of Standard Reference Materials. Standard reference materials are analyzed at regular intervals to ensure accurate recoveries by the analytical methodologies. Present policy requires the analysis of EPA reference samples on a biannual basis for all parameters contained in the ampoules. Metals analyses by ICP instrumentation are checked at least once per week utilizing the diluted EPA reference ampoules. Recoveries for all legal sample analyses are monitored using EPA reference checks. The accuracy of the analysis for mercury in fish tissues for the Fresh Water Institute QA/QC program and for

client submitted samples is monitored using NBS Tuna Reference Material. Speciality analyses for selected metals in unusual matrices are monitored using NBS or equivalent materials to ensure adequate recovery of the desired chemical species.

Analysis of Blind Duplicates. On an irregular and unannounced basis, replicate samples are submitted to the laboratory to determine the precision of the entire sample submission, sample analysis, report production, and data validation procedure. The blind nature of the submission to the laboratory assists in evaluating the established procedure for submitting samples and obtaining analytical results. Presently only routine parameters have been checked using blind duplicates, however, plans exist to expand the program to include the majority of parameters analyzed by the Water Analysis Laboratory.

Participation In Internal and External Collaborative Studies. The Water Analysis Laboratory participates in a comprehensive selection of internal and external interlaboratory split sample, round-robin studies. Almost all of the analytical tests performed by the laboratory are scrutinized through participation in one or more of the following collaborative studies.

1. Alberta Water Analysts Committee
2. Interregional Quality Control - Prairie Provinces Water Board Interlabs.
3. Fresh Water Institute Mercury in Fish Quality Control Program
4. Long Range Transport of Atmospheric Pollutants Quality Control Program
5. Lake Diefenbaker Quality Control Study
6. Participation in miscellaneous industrial, municipal, and private sector laboratory intercomparisons.

Participation in the above studies includes private sector, municipal, industrial, university, provincial, and federal government laboratories within Alberta and across Canada.

The performance of the Water Analysis Laboratory in round-robin studies has continued to improve with increased participation in QA/QC activities.

Comprehensive Calibration Check. On a once per year basis, a comprehensive calibration check is completed for all parameters routinely analyzed in the Water Analysis Laboratory. In January when sample submissions are at minimum levels, the slope, linearity and detection limit of each analytical system are checked using a complete series of new standards and replicate measurements of the blank. An accurate calibration is verified by independent QC solutions and the analysis of standard reference materials. Adequate recoveries (within ± 5%) of reference materials are essential before proceeding with the analysis of samples.

Although this program is relatively new to the laboratory, recoveries of standard reference materials have consistently remained between 90 - 110% for almost all parameters.

QA/QC Studies of Support Apparatus. Random checks to determine positive and negative contamination effects are completed on an unscheduled basis. Sample containers including caps and lids as well as lid liners are examined for contributory contamination effects by storing and/or soaking the apparatus in distilled deionized water for a period of up to 1 week. Quantitative analysis of the extraction fluid confirms the presence or absence of contamination effects. This QC check is repeated using standards of known concentration to determine the possibility of analyte absorption onto the walls of the sample container apparatus or analyte absorption into or desorption from the pores of the cap or lid system.

Similar positive and negative contamination checks are conducted on filter papers that are routinely used to remove particulates from samples. Distilled deionized water rinses of the filter paper and the filter support apparatus are analyzed for positive contaminants. This QC check is repeated using standards of known concentration to measure adsorption effects of the filter paper apparatus.

Reagents utilized to prepare preservatives are also analyzed to confirm the absence of detectable contaminants. After the preservative ampoules are prepared and sealed, the contents of three randomly selected ampoules per box of 144 ampoules are extracted, diluted to 500 mL and analyzed for each element pertinent to the preservative.

The A, B Quality Control Technique. The A,B technique for interlaboratory control of calibration is based upon the Youden technique for detecting systematic error in evaluating interlaboratory comparability (1). Mr. Don King of the Ontario Ministry of the Environment (2) has adapted Youden's technique to control calibration and detect systematic error on a daily or analytical run basis. The simplicity of the technique is demonstrated by the basic mathematics and the minimum number of quality control solutions required for analysis as described below.

1. A blank (B1) and two standards (A and B) of known concentration values, designed to provide analytical results within the normal operating range of the methodology, are prepared from an independent reference material and analyzed once per analytical run or batch of samples immediately after the instrument has been completely calibrated.
2. After blank correction, the two results QCA and QCB, as well as their sum (A+B) and their difference (A-B), are recorded. A sequential plot of these values is maintained over time.
3. The standard deviation (s) of accumulated A, B data from historical records can be utilized to estimate and set control limits within which the individual points (A+B) and (A-B) are expected to fall according to statistical averages. Therefore:

$$\text{WARNING LIMITS} = (\overline{A+B}) \pm 2s \text{ and } (\overline{A-B}) \pm 2s$$

$$\text{CONTROL LIMITS} = (\overline{A+B}) \pm 3s \text{ and } (\overline{A-B}) \pm 3s.$$

Graphical representation of A, B control limits includes:

	A + B LIMITS	A - B LIMITS
UPPER CONTROL LIMIT	$(\overline{A+B}) + 3s$	$(\overline{A-B}) + 3s$
UPPER WARNING LIMIT	$(\overline{A+B}) + 2s$	$(\overline{A-B}) + 2s$
MEAN	$(\overline{A+B})$	$(\overline{A-B})$
LOWER WARNING LIMIT	$(\overline{A+B}) - 2s$	$(\overline{A-B}) - 2s$
LOWER CONTROL LIMIT	$(\overline{A+B}) - 3s$	$(\overline{A-B}) - 3s$.

Since the quality control solutions are analyzed during each analytical run, a historical record of the recovery of each solution is obtained. Once the true or accepted value for a quality control solution is obtained, an analyst can verify the instrument calibration within the originally defined performance limits established for the analytical system. Decisions by the analyst on between-run calibration changes and within-run sensitivity changes are based upon at least two information sources.

During method development, sufficient investigations should have been undertaken to ensure that the response of the analytical technique and the instrumentation to the chemical parameter follows established physical and/or chemical laws in a relatively stable and predictable fashion. Sudden changes in the slope and/or intercept of the calibration curve are unexpected events that are usually indicative of an error in the preparation of the standards, degradation of reagents, or a malfunction of the instrumentation.

When a calibration curve is prepared and compared with previously acceptable curves, agreement of slope and intercept is usually confirmed by analyzing quality control solutions. When a change in instrument response is observed a decision within the bounds of these four alternatives is required.

i. To decide correctly that no change in calibration is required.

ii. To decide correctly that a change in calibration is required

iii. To decide incorrectly that a change in calibration is required (TYPE I ERROR).

iv. To decide incorrectly that no change in calibration is required (TYPE II ERROR).

Since small changes in slope and intercept (within specified limits) are necessarily inherent in any measuring system, the analyst must recognize and accept normal variability to avoid introducing TYPE I ERROR. TYPE II errors occur infrequently since large changes in calibration (slope and/or intercept) are not expected and require positive confirmation. TYPE I error is highly probable if a suspected change in calibration is not confirmed by an alternative, independent QC check. Systematic error is generally the result of a decision to change the calibration based upon the unsupported evidence of

the accuracy of a new batch of standards, reagents and instrument set-up. The A, B quality control technique provides the necessary continuity of data required to assist the analyst in making a proper decision on accurate calibration.

Warning Limits surrounding the mean value are established at the 95% confidence interval to ensure that the limits will be exceeded by chance less than 5% of the time. Control Limits are established at the 99% confidence level to ensure that the limits will be exceeded by chance less than 1% of the time.

4. Any (A+B) data point falling outside of the Control Limits identifies a probable significant systematic error in calibration. Before proceeding with the analysis of samples, the source of the error must be identified and corrected. Samples must not be analyzed until the analytical system is properly calibrated and the QC solutions verify that the analytical system generates results within the control limits established for the system.
5. Any individual (A-B) data point falling outside of the Control Limits is usually the result of gross random error in either A or B which strongly suggests that the precision of the method has degraded. Usually each quality control solution is carried through the entire analytical process. However, separate A, B control solutions may be used for instrument calibration while recovery check solutions may be used to confirm reproducible digestion processes.

QUALITY CONTROL DATA

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; no preservatives are added.

SAMPLE PREPARATION: An aliquot of unfiltered, supernatant sample is weighed for analysis.

ANALYTICAL PROCEDURE: Automated potentiometric titration method of determining the phenolphthalein alkalinity (pH 8.3) and total alkalinity (pH 4.5) by titration of an unfiltered aliquot of sample with a standard solution of sulfuric acid.

INSTRUMENTATION: An automatic potentiometric titrator such as Fisher Titralyzer or Metrohm Titration System including a sample holder, potentiometer, automatic burette, titroprocessor and digital printer completes the series of titrations.

ANALYTICAL RANGE: 5-1200 mg/L LOWEST REPORTED VALUE: <5 mg/L

CALIBRATION: 3 standards RESULTS REPORTED TO NEAREST: 1 mg/L

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
750	250	1000±18	1000±12	496±12	496±8

WITHIN-RUN STD DEVIATION: 2.8 BETWEEN-RUN STD DEVIATION: 3.6

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	114	155	21
STANDARD DEVIATION	0.7	1.1	2.2
PRECISION (% RSD)	0.6	0.2	0.2

DETECTION LIMIT: 2 mg/L $CaCO_3$

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
65.3	68.0	104
81.8	84.0	102
75.8	77.0	102

COMMENTS: Chemical components contributing to alkalinity may irreversibly precipitate in stored samples. Alkalinity and pH analyzed on same aliquot of sample.

ALKALINITY, Total
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	750	250	1000 ± 12.9	1000 ± 8.6	497 ± 9.2	497 ± 6.2	2.2	2.6
1983	750	250	1001 ± 19.8	1001 ± 13.2	497 ± 13.7	497 ± 9.2	3.2	4.0
1984	750	250	1003 ± 9.5	1004 ± 6.3	500 ± 6.6	500 ± 4.4	1.6	1.9
1985	750	250	1004 ± 10.7	1004 ± 7.1	500 ± 7.1	500 ± 4.8	1.7	2.1
1986	750	250	986 ± 13.0	986 ± 9.0	490 ± 13.9	490 ± 9.0	2.8	3.0

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	84	143	16	0.39	1.62	1.01	0.61	0.35	0.11	1
1983	269	298	38	1.00	1.89	4.54	1.14	0.37	0.50	3
1984	93	170	20	0.92	1.26	1.45	0.68	0.25	0.15	3
1985	142	353	58	0.64	1.07	2.23	0.45	0.22	0.23	2
1986	155	288	119	0.95	1.15	1.62	1.2	0.28	0.22	3

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	74.7	76.9	103
	21.7	20.7	95
	16.0	17.0	106
1983	73.7	75.2	102
1984	16.0	18.0	112
	73.7	74.2	101
1985	73.7	73.3	100
	73.7	75.0	102
1986	64.7	64.0	99
	41.1	42.0	102

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; field preserve with 5 mL of 50% HNO_3 (blue dot ampoule).

SAMPLE PREPARATION: The pH of a 100 mL aliquot of sample in a 200 mL flask is adjusted to 4.8 (mixed methyl red-bromphenol blue indicator) using H_2SO_4. Add ammonium tartrate buffer to adjust the pH to 6.5.

ANALYTICAL PROCEDURE: Add 8-hydroxyquinoline in acetylacetone and ethyl propionate to extract aluminum into the solvent layer. Mix the 2 phase solution for 10 minutes, allow organic layer to separate and float the organic layer into the neck of the volumetric flask using distilled water. A glass wool plug is utilized to remove visible particulates in the solvent layer.

INSTRUMENTATION: A Perkin-Elmer 603 atomic absorption spectrophotometer measures the absorbance at 309.2 nm. A stripchart recorder displays the sample peaks.

ANALYTICAL RANGE: 0.02-1 mg/L Al LOWEST REPORTED VALUE: <0.02 mg/L Al

CALIBRATION: 6 standards RESULTS REPORTED TO NEAREST: 0.01 mg/L Al

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A+B)}$ LIMITS		$\overline{(A-B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.80	0.20	1.00±0.11	1.00±0.076	0.59±0.085	0.59±0.057

WITHIN-RUN STD DEVIATION: 0.020 BETWEEN-RUN STD DEVIATION: 0.024

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	33	13	6
STANDARD DEVIATION	0.0088	0.021	0.029
PRECISION (% RSD)	10.2	5.6	4.6

DETECTION LIMIT: 0.026 mg/L Al

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.365	0.363	99
0.500	0.525	105
0.729	0.753	103

COMMENTS:

ALUMINUM, Extractable
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	1.50	0.40	1.85 ±0.35	1.85 ±0.23	1.04 ±0.24	1.04 ±0.16	0.056	0.071
1984	1.50	0.40	1.90 ±0.27	1.90 ±0.18	1.01 ±0.28	1.01 ±0.19	0.066	0.065
1985	1.50	0.50	2.02 ±0.17	2.02 ±0.11	0.99 ±0.13	0.99 ±0.09	0.032	0.036
1986	1.50	0.50	2.02 ±0.24	2.02 ±0.16	0.99 ±0.19	0.99 ±0.12	0.044	0.051

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	-	-	-	-	-	-	-	-	-	-
1983	70	6	6	.013	.042	.40	15.3	7.1	2.7	0.039
1984	93	11	1	.011	.036	.035	9.6	5.3	3.0	0.033
1985	65	9	6	.012	.021	.016	13.1	3.6	0.98	0.036
1986	53	9	2	.016	.041	.022	12.0	5.6	1.6	0.047

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	0.020	0.020	100
1983	0.59	0.53	90
	1.96	1.84	94
1984	0.091	0.090	99
	0.54	0.52	96
1985	0.036	0.037	103
	0.50	0.53	106
1986	0.054	0.052	96
	0.50	0.52	104

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; field preserve with 5 mL of 50% HNO_3 (blue dot ampoule).

SAMPLE PREPARATION: An aliquot of unfiltered sample is manually digested with HNO_3 and H_2SO_4 until SO_3 fuming occurs. $HClO_4$ is added and heated until fuming occurs.

ANALYTICAL PROCEDURE: In an automated system, an aliquot of digested sample is mixed with 50% HCl and $NaBH_4$ reagent which reduces inorganic arsenic compounds to arsine (AsH_3) gas which is stripped from the solution and passed into a heated (900°C) tube furnace.

INSTRUMENTATION: The absorbance of ground state arsenic is measured at 193.7 nm using an Instrumentation Laboratory Video 22 dual channel atomic absorption spectrophotometer. A stripchart recorder displays the peaks.

ANALYTICAL RANGE: 0.0001-0.0050 mg/L As LOWEST REPORTED VALUE: <0.0001 mg/L As

CALIBRATION: 6 standards RESULTS REPORTED TO NEAREST: 0.0001 mg/L As

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.0040	0.0010	0.0492 ± 0.0009	0.0049 ± 0.0006	0.0027 ± 0.0010	0.0027 ± 0.0007

WITHIN-RUN STD DEVIATION: 0.0002 BETWEEN-RUN STD DEVIATION: 0.0002

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	32	18	2
STANDARD DEVIATION	0.0001	0.0002	0.0004
PRECISION (% RSD)	28.6	14.0	16.0

DETECTION LIMIT: 0.0003 mg/L As

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.0500	0.0530	106
0.0100	0.0105	105

COMMENTS: Arsenic is simultaneously analyzed with selenium.

ARSENIC, Total
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	0.0075	0.0025	0.0099 ±0.0011	0.0099±0.0007	0.0049±0.0008	0.0049±0.0006	0.0002	0.0002
1983	0.0075	0.0025	0.0107 ±0.0018	0.0107±0.0012	0.0054±0.0014	0.0054±0.0009	0.0004	0.0004
1984	0.0075	0.0025	0.0109 ±0.0010	0.0109±0.0006	0.0054±0.0008	0.0054±0.0005	0.0002	0.0002
1985	0.0075	0.0025	0.0103 ±0.0010	0.0103±0.0007	0.0051±0.0006	0.0051±0.0004	0.0001	0.0003
1986	0.0038	0.0012	0.0050 ±0.0005	0.0050±0.0003	0.0025±0.0003	0.0025±0.0002	0.0001	0.0001

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	LIMIT, mg/L
1982	6	23	30	0.0824	0.1322	0.2165	5.3	5.3	3.2	0.25
1983	43	35	6	0.0001	0.0001	0.0006	17.3	8.6	17.9	0.0003
1984	16	-	2	0.0005	-	0.0004	6.9	-	4.9	0.0002
1985	42	17	9	0.0004	0.0001	0.0003	6.4	7.8	5.6	0.0001
1986	26	14	5	0.0001	0.0002	0.0004	13.0	12.9	11.1	0.0003

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	0.258	0.240	93
	0.040	0.047	120
1983	0.0030	0.0034	113
	0.0180	0.0180	100
	0.0600	0.0630	105
1984	0.0030	0.0034	113
1985	0.0044	0.0046	104
1986	0.0025	0.0024	96
	0.0134	0.0130	97

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; field preserve with 5 mL of 50% HNO_3 acid (blue dot ampoule).

SAMPLE PREPARATION: A 50 mL aliquot of unfiltered sample is manually digested in a Kjeldahl flask with a mixture of HNO_3 and HCl acids at low heat and evaporated almost to dryness. After cooling, add 10 mL of 10% HCl to dissolve any residue. The sample is transferred to a culture tube for centrifugation to remove suspended materials.

ANALYTICAL PROCEDURE: Automated atomic emission spectrometry by direct aspiration into a high temperature (approximately 6500°K) argon plasma.

INSTRUMENTATION: A JARRELL-ASH (975 PLASMA ATOMCOMP) simultaneous multielement (26 channels) Inductively Coupled Argon Plasma Atomic Emission Spectrometer (ICAP-AES) with PDP-8 microprocessor and Digital Decwriter II printer.

SPECTRAL LINE: 493.4 nm

ANALYTICAL RANGE: 0.001-0.5 mg/L Ba LOWEST REPORTED VALUE: <0.001 mg/L Ba

CALIBRATION: 1 standard RESULTS REPORTED TO NEAREST: 0.001 mg/L Ba

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A+B)}$ LIMITS		$\overline{(A-B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.400	0.100	0.500±0.034	0.500±0.023	0.303±0.030	0.303±0.020

WITHIN-RUN STD DEVIATION: 0.007 BETWEEN-RUN STD DEVIATION: 0.008

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	75	12	2
STANDARD DEVIATION	0.0018	0.0097	0.014
PRECISION (% RSD)	4.8	6.8	4.3

DETECTION LIMIT: 0.005 mg/L Ba

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.456	0.434	95
1.7	1.65	97
119.6	119.	100

COMMENTS: Methodology for barium analysis implemented in 1986; therefore, no previous data available. All ICAP heavy metal parameters, with the exception of boron, are determined simultaneously in a single aliquot of sample.

BARIUM, Total
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	-	-	-	-	-	-	-	-
1984	-	-	-	-	-	-	-	-
1985	-	-	-	ANALYSIS INITIATED IN 1986			-	-
1986	0.400	0.100	0.489±0.044	0.489±0.029	0.294±0.043	0.294±0.028	0.010	0.010

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	-	-	-	-	-	-	-	-	-	-
1983	-	-	-	-	-	-	-	-	-	-
1984	-	-	-	-	-	-	-	-	-	-
1985	-	-	-	-	ANALYSIS INITIATED IN 1986			-		-
1986	67	17	3	0.004	0.008	0.006	5.8	6.1	1.4	0.01

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	-	-	-
1983	-	-	-
1984	-	-	-
1985	-	ANALYSIS INITIATED IN 1986	-
1986	1.7	1.7	100
	0.46	0.45	98

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; field preserve with 5 mL of 50% HNO_3 acid (blue dot ampoule).

SAMPLE PREPARATION: A 50 mL aliquot of unfiltered sample is manually digested in a Kjeldahl flask with a mixture of HNO_3 and HCl acids at low heat and evaporated almost to dryness. After cooling, add 10 mL of 10% HCl to dissolve any residue. The sample is transferred to a culture tube for centrifugation to remove suspended materials.

ANALYTICAL PROCEDURE: Automated atomic emission spectrometry by direct aspiration into a high temperature (approximately 6500°K) argon plasma.

INSTRUMENTATION: A JARRELL-ASH (975 PLASMA ATOMCOMP) simultaneous multielement (26 channels) Inductively Coupled Argon Plasma Atomic Emission Spectrometer (ICAP-AES) with PDP-8 microprocessor and Digital Decwriter II printer.

SPECTRAL LINE: 313.0 nm

ANALYTICAL RANGE: 0-0.5 mg/L Be LOWEST REPORTED VALUE: <0.001 mg/L Be

CALIBRATION: 1 standard RESULTS REPORTED TO NEAREST: 0.001 mg/L Be

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.400	0.100	0.488±0.029	0.488±0.019	0.298±0.029	0.298±0.019

WITHIN-RUN STD DEVIATION: 0.007 BETWEEN-RUN STD DEVIATION: 0.007

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	16	1	-
STANDARD DEVIATION	0.0004	0.0028	-
PRECISION (% RSD)	33.1	1.3	-

DETECTION LIMIT: 0.001 mg/L Be

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.05	0.048	96
0.10	0.096	96
0.20	0.184	92

COMMENTS: All ICAP heavy metal parameters, with the exception of boron, are determined simultaneously in a single aliquot of sample.

BERYLLIUM, Total
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	0.020	0.800	0.804 ±0.112	0.804 ±0.074	0.767±0.106	0.767 ±0.071	0.025	0.026
1984	0.800	0.020	0.792 ±0.066	0.792 ±0.044	0.757±0.062	0.757 ±0.041	0.015	0.015
1985	0.800	0.020	0.752 ±0.105	0.752 ±0.070	0.717±0.100	0.717 ±0.067	0.023	0.024
1986	0.400	0.100	0.482 ±0.027	0.482 ±0.018	0.292±0.022	0.292 ±0.015	0.005	0.006

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	-	-	-	-	-	-	-	-	-	-
1983	-	1	-		0.0007	-	-	0.61	-	-
1984	1	-	-	0.0007	-	-	12.8	-	-	0.002
1985	1	-	-	0.0007	-	-	47.1	-	-	0.002
1986	4	1	-	0.004	0.008	-	28.1	3.9	-	0.012

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	0.010	0.009	90
	0.750	0.684	91
1983	0.020	0.017	85
	0.250	0.261	104
	0.900	0.779	87
1984	0.250	0.201	80
	0.900	0.796	88
1985	0.180	0.150	83
1986	0.118	0.104	95
	0.235	0.219	93
	0.470	0.443	94

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; no preservatives are added.

SAMPLE PREPARATION: An aliquot of sample is filtered through 0.45 micron membrane filter paper at the laboratory.

ANALYTICAL PROCEDURE: Automated atomic emission spectrometry by direct aspiration into a high temperature (approximately 6500°K) argon plasma.

INSTRUMENTATION: A JARRELL-ASH (975 PLASMA ATOMCOMP) simultaneous multielement (26 channels) Inductively Coupled Argon Plasma Atomic Emission Spectrometer (ICAP-AES) with PDP-8 microprocessor and Digital Decwriter II printer.

SPECTRAL LINE: 249.7 nm

ANALYTICAL RANGE: 0-1.0 mg/L B LOWEST REPORTED VALUE: <0.001 mg/L B

CALIBRATION: 1 standard RESULTS REPORTED TO NEAREST: 0.001 mg/L B

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.750	0.250	0.998±0.052	0.998±0.035	0.494±0.021	0.494±0.014

WITHIN-RUN STD DEVIATION: 0.005 BETWEEN-RUN STD DEVIATION: 0.009

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	20	6	2
STANDARD DEVIATION	0.0042	0.0057	0.0057
PRECISION (% RSD)	11.9	1.5	1.0

DETECTION LIMIT: 0.013 mg/L B

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.750	0.748	100
0.250	0.252	101

COMMENTS: This method was implemented in 1986. An aliquot of sample from a plastic bottle is analyzed for boron as a single element ICAP parameter.

BORON, Filtered
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982								
1983								
1984								
1985	ANALYSIS INITIATED IN 1986							
1986	0.400	0.100	1.008 ± 0.028	1.008 ± 0.019	0.492 ± 0.022	0.492 ± 0.015	0.005	0.006

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982										
1983										
1984										
1985	ANALYSIS INITIATED IN 1986									
1986	15	3	1	0.005	0.009	0.02	21.5	3.6	2.9	0.015

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982			
1983			
1984			
1985	ANALYSIS INITIATED IN 1986		
1986	0.750 0.250	0.742 0.252	99 101

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; field preserve with 5 mL of 50% HNO_3 acid (blue dot ampoule).

SAMPLE PREPARATION: A 50 mL aliquot of unfiltered sample is manually digested in a Kjeldahl flask with a mixture of HNO_3 and HCl acids at low heat and evaporated almost to dryness. After cooling, add 10 mL of 10% HCl to dissolve any residue. The sample is transferred to a culture tube for centrifugation to remove suspended materials.

ANALYTICAL PROCEDURE: Automated atomic emission spectrometry by direct aspiration into a high temperature (approximately 6500°K) argon plasma.

INSTRUMENTATION: A JARRELL-ASH (975 PLASMA ATOMCOMP) simultaneous multielement (26 channels) Inductively Coupled Argon Plasma Atomic Emission Spectrometer (ICAP-AES) with PDP-8 microprocessor and Digital Decwriter II printer.

SPECTRAL LINE: 228.8 nm

ANALYTICAL RANGE: 0-0.5 mg/L Cd LOWEST REPORTED VALUE: <0.001 mg/L Cd

CALIBRATION: 1 standard RESULTS REPORTED TO NEAREST: 0.001 mg/L Cd

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.400	0.100	0.503±0.034	0.503±0.023	0.304±0.030	0.304±0.020

WITHIN-RUN STD DEVIATION: 0.007 BETWEEN-RUN STD DEVIATION: 0.008

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	63	2	-
STANDARD DEVIATION	0.0007	0.0053	-
PRECISION (% RSD)	23.5	2.8	-

DETECTION LIMIT: 0.002 mg/L Cd

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.013	0.013	100
0.025	0.026	104
0.050	0.049	98

COMMENTS: All ICAP heavy metal parameters, with the exception of boron, are determined simultaneously in a single aliquot of sample.

CADMIUM, Total
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	0.020	0.800	0.821 ±0.127	0.821 ±0.085	0.775±0.125	0.775 ±0.083	0.030	0.030
1984	0.800	0.020	0.817 ±0.030	0.817 ±0.020	0.780±0.026	0.780 ±0.017	0.006	0.007
1985	0.800	0.020	0.797 ±0.106	0.797 ±0.071	0.759±0.103	0.759 ±0.069	0.020	0.025
1986	0.400	0.100	0.489 ±0.140	0.489 ±0.094	0.291±0.139	0.291 ±0.093	0.030	0.033

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	LIMIT,mg/L
1982	-	-	-	-	-	-	-	-	-	-
1983	56	3	-	0.0006	0.0044	-	9.8	2.9	-	0.002
1984	50	6	-	0.001	0.002	-	7.4	1.3	-	0.003
1985	89	7	3	0.0008	0.0036	0.011	12.0	2.1	2.2	0.002
1986	54	-	-	0.0008	-	-	15.5	-	-	0.002

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	0.0135	0.0130	96
	0.0500	0.0490	98
1983	0.0025	0.0025	100
	0.013	0.014	108
	0.070	0.073	104
1984	0.013	0.013	100
	0.070	0.077	110
1985	0.014	0.015	107
	0.044	0.041	93
1986	0.020	0.022	109
	0.039	0.039	100
	0.078	0.081	104

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; no preservatives are added.

SAMPLE PREPARATION: At the laboratory, a 10 mL aliquot of filtered sample is acidified with 0.5 mL of 50% HNO_3.

ANALYTICAL PROCEDURE: Automated atomic absorption method in which an aliquot of acidified sample is mixed with lanthanum chloride solution and aspirated into an air-acetylene flame.

INSTRUMENTATION: The absorbance of calcium is measured at 422.7 nm using an IL 251 atomic absorption spectrophotometer. A stripchart recorder displays the peaks.

ANALYTICAL RANGE: 1-200 mg/L Ca LOWEST REPORTED VALUE: <1 mg/L Ca

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 1 mg/L Ca

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
50	150	203±10	203±7	100.5±7	100.5±5

WITHIN-RUN STD DEVIATION: 2 BETWEEN-RUN STD DEVIATION: 2

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	116	82	28
STANDARD DEVIATION	0.6	1.4	3.1
PRECISION (% RSD)	15.1	2.3	2.1

DETECTION LIMIT: 2 mg/L Ca

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
20.0	20.3	102
40.0	41.8	104

COMMENTS: Direct calcium analysis by automated AAS implemented in 1981, (NAQUADAT #20110). Acidification of sample aliquot was implemented on August 15, 1985 to avoid precipitation during storage. Calcium and magnesium are analyzed from the same aliquot of sample.

CALCIUM, Filtered
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	50	150	214 ± 29	217 ± 19	106 ± 15	106 ± 10	4	5
1983	50	150	200 ± 13	200 ± 9	99 ± 9	99 ± 6	2	3
1984	50	150	199 ± 12	199 ± 8	99 ± 9	99 ± 6	2	2
1985	50	150	201 ± 15	201 ± 10	100 ± 11	100 ± 7	3	3
1986	50	150	202 ± 12	202 ± 8	100 ± 9	100 ± 6	2	2

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	150	145	65	1	2	3	9.5	2.9	2.4	3
1983	136	99	36	1	2	4	7.7	2.8	2.9	3
1984	103	86	40	1	2	4	8.6	2.6	2.9	3
1985	123	102	25	1	1	3	6.9	2.3	2.1	3
1986	96	176	39	1	3	4	10.0	4.4	3.1	3

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	6.7	6.0	90
	32.0	30.0	94
1983	32.0	33.0	103
1984	28.3	28.5	101
	42.5	42.4	100
1985	40.6	42.0	103
1986	42.4	43.0	101
	67.9	68.0	100

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 125 mL polyethylene bottle; keep cool (4°C) and out of direct sunlight.

SAMPLE PREPARATION: Unfiltered sample is mixed prior to pouring an aliquot for analysis.

ANALYTICAL PROCEDURE: In the automated phenolphthalein colorimetric method an aliquot of sample is sparged in an acid medium which converts inorganic carbonates to CO_2 gas. After dialysis, the CO_2 concentration is determined by measuring the loss of color in a borate buffered alkaline phenolphthalein solution.

INSTRUMENTATION: A Technicon AutoAnalyzer II system with a 50 mm flow cell and a 6 inch gas dialysis membrane measures the loss of color at 550 nm. A stripchart recorder displays the sample peaks.

ANALYTICAL RANGE: 1-80 mg/L C LOWEST REPORTED VALUE: <1 mg/L C

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 1 mg/L C

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
20	60	81 ± 5	81 ± 3	39.7±2	39.7±1

WITHIN-RUN STD DEVIATION: 0.5 BETWEEN-RUN STD DEVIATION: 0.9

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	19	39	41
STANDARD DEVIATION	0.29	0.39	0.54
PRECISION (% RSD)	14.7	1.4	1.0

DETECTION LIMIT: 1 mg/L C

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
15.9	16.4	103
17.9	20.8	116
19.7	20.2	102

COMMENTS: This carbon method was implemented in 1981. Results reflect supernatant inorganic carbon which is simultaneously analyzed with dissolved organic carbon.

CARBON, INORGANIC, Dissolved
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER						STD. DEVIATION	
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	WITHIN RUN	BETWEEN RUN
1982	60.0	20.0	78.8± 5.1	78.8± 3.4	40.0± 2.4	40.0± 1.6	0.6	0.9
1983	60.0	20.0	81.1± 9.3	81.1± 6.2	40.1± 6.0	40.1± 4.0	1.4	1.8
1984	60.0	20.0	80.7± 5.1	80.7± 3.4	40.2± 3.2	40.2± 2.1	0.8	1.0
1985	20.0	60.0	82.3± 11.2	82.3± 7.4	40.8± 6.8	40.8± 4.5	1.6	2.2
1986	20.0	60.0	81.7± 4.7	81.7± 3.2	39.5± 3.7	39.5± 2.5	0.8	1.0

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	-	-	-	-	-	-	-	-	-	-
1983	46	102	53	0.45	0.55	1.06	5.49	2.34	1.91	1
1984	22	52	38	0.41	0.49	0.52	3.39	1.81	1.01	1
1985	12	49	33	0.44	0.49	0.51	7.49	1.76	0.92	1
1986	21	48	35	0.49	0.46	0.92	6.9	1.8	1.5	2

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	-	-	-
1983	-	-	-
1984	19.2	19.3	101
	40.4	40.3	100
1985	19.1	16.0	84
	23.0	19.4	84
1986	19.4	18.3	94
	19.7	18.3	93

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 125 mL polyethylene bottle; keep cool (4°C) and out of direct sunlight.

SAMPLE PREPARATION: Unfiltered sample is mixed prior to pouring an aliquot for analysis.

ANALYTICAL PROCEDURE: In the automated phenolphthalein colorimetric method, inorganic carbon is removed by sparging of the acidified sample using nitrogen gas to remove CO_2. An acid-persulfate-UV digestion converts dissolved organic constituents to CO_2 gas.

INSTRUMENTATION: A Technicon AutoAnalyzer II system with a 50 mm flow cell and a 6 inch gas dialysis membrane measures the loss of color at 550 nm in a borate buffered alkaline phenolphthalein solution. A stripchart recorder displays the sample peaks.

ANALYTICAL RANGE: 0.4-24 mg/L C LOWEST REPORTED VALUE: <0.4 mg/L C

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 0.1 mg/L C

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
6.0	18.0	24.1±1.1	24.1±0.7	11.8±1.0	11.8±0.7

WITHIN-RUN STD DEVIATION: 0.2 BETWEEN-RUN STD DEVIATION: 0.3

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	28	65	20
STANDARD DEVIATION	0.1	0.2	0.3
PRECISION (% RSD)	18.6	2.4	1.9

DETECTION LIMIT: .3 mg/L C

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
20.6	18.9	92
91.8	93.6	102

COMMENTS: This carbon method was implemented in 1981. Results reflect supernatant organic carbon which is simultaneously analyzed with dissolved inorganic carbon. Total organic carbon = particulate carbon + dissolved organic carbon.

CARBON, ORGANIC Dissolved
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $(\overline{A+B})\pm 3s$	WARNING LIMITS $(\overline{A+B})\pm 2s$	CONTROL LIMITS $(\overline{A-B})\pm 3s$	WARNING LIMITS $(\overline{A-B})\pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	18.0	6.0	24.5 ± 1.2	24.5 ± 0.8	12.1 ± 1.1	12.1 ± 0.7	0.3	0.3
1983	18.0	6.0	24.2 ± 2.0	24.2 ± 1.3	12.2 ± 1.6	12.2 ± 1.1	0.4	0.4
1984	18.0	6.0	24.4 ± 1.2	24.4 ± 0.8	12.1 ± 0.9	12.1 ± 0.6	0.2	0.2
1985	18.0	6.0	24.2 ± 2.4	24.2 ± 1.6	12.1 ± 1.0	12.1 ± 0.7	0.2	0.4
1986	18.0	6.0	24.0 ± 2.5	24.0 ± 1.7	11.7 ± 1.5	11.7 ± 1.0	0.4	0.5

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	-	-	-	-	-	-	-	-	-	-
1983	32	42	44	0.2	0.2	0.4	14.9	2.9	2.0	0.6
1984	27	30	26	0.2	0.4	0.3	11.1	4.4	1.5	0.6
1985	25	21	32	0.2	0.3	0.3	13.4	3.4	1.6	0.6
1986	35	38	30	0.3	0.3	0.4	13.5	4.1	0.8	0.9

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	16.0	15.7	98
	64.0	64.0	100
	75.8	78.7	104
1983	4.1	4.3	105
	75.8	78.0	103
1984	11.9	10.6	89
	23.7	20.6	87
	61.2	63.6	104
1985	4.0	3.9	98
	8.0	8.1	101
1986	61.3	69.4	113
	61.3	64.4	105
	91.8	93.6	102

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 125 mL polyethylene bottle; keep cool (4°C) and out of direct sunlight.

SAMPLE PREPARATION: Unfiltered sample is mixed prior to filtering an aliquot through precleaned and preheated to 500°C GFC glass fibre filter paper (Whatman GF/C).

ANALYTICAL PROCEDURE: In the thermal combustion method, particulate carbon compounds are oxidized to CO_2 at 1030°C in the presence of Co_3O_4 + Ag and Cr_2O_3 catalysts. A cyclohexanone-2,4-dinitrophenyl hydrazone combined carbon and nitrogen standard is used to calibrate the analytical system.

INSTRUMENTATION: A Carlo-Erba Model 1106 CHN Analyzer with a thermal conductivity detector measures the amount of carbon present in the particulate fraction. An electronic integrator displays the chromatogram and provides a printout of the analytical results.

ANALYTICAL RANGE: 0.02-100 mg/L C LOWEST REPORTED VALUE: <0.02 mg/L C

CALIBRATION: 1 standard RESULTS REPORTED TO NEAREST: 0.01 mg/L C

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
		N/A			

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	124	2	4
STANDARD DEVIATION	0.21	4.3	4.6
PRECISION (% RSD)	13.7	9.6	3.9

DETECTION LIMIT: 0.63 mg/L C

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
10.48	10.62	101
18.44	17.78	96
38.67	37.76	98

COMMENTS: This method was implemented in 1983. An aliquot of sample is filtered for particulate nitrogen and particulate carbon (simultaneous analysis) upon receipt at the laboratory. Large floating particles are excluded from the aliquot of sample.

CARBON, Particulate
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982								
1983								
1984				N/A				
1985								
1986								

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	-	-	-	-	-	-	-	-	-	-
1983	30	2	1	0.44	1.21	0.74	16.8	3.5	1.3	1.3
1984	85	4	3	0.28	1.87	3.80	14.1	6.6	5.0	0.84
1985	88	4	-	0.19	1.69	-	15.9	5.1	-	0.57
1986	96	6	1	0.31	2.46	5.09	14.5	6.9	4.1	0.93

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	-	-	-
1983	19.0	19.4	102
	30.3	30.5	101
	66.0	64.2	97
1984	13.3	13.2	99
	22.8	21.9	96
	47.9	49.3	103
1985	9.25	9.44	102
	16.2	16.3	101
	35.5	35.0	99
1986	12.1	11.6	96
	20.6	20.0	97
	44.2	44.2	100

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; no preservatives are added.

SAMPLE PREPARATION: An aliquot of sample is filtered through 0.45 micron membrane filter paper at the laboratory.

ANALYTICAL PROCEDURE: In the automated ferricyanide colorimetric method, an aliquot of sample is mixed with mercuric thiocyanate which liberates SCN^- which combines with ferric ion to produce a red colored complex.

INSTRUMENTATION: A Technicon AutoAnalyzer II system with a 15 mm flow cell measures the absorbance of the red colored complex at 480 nm. A stripchart recorder displays the sample peaks.

ANALYTICAL RANGE: 1-100 mg/L Cl LOWEST REPORTED VALUE: <1 mg/L Cl

CALIBRATION: 6 standards RESULTS REPORTED TO NEAREST: 1 mg/L Cl

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
25	75	101 ± 5	101.3 ± 3	51 ± 4	51 ± 3

WITHIN-RUN STD DEVIATION: 1 BETWEEN-RUN STD DEVIATION: 1

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	178	39	19
STANDARD DEVIATION	0.2	0.5	0.8
PRECISION (% RSD)	12.2	1.7	0.9

DETECTION LIMIT: 1 mg/L Cl

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
51.7	51.5	100
40.0	40.9	102

COMMENTS: Loss of linearity in calibration curve above 50 mg/L Cl. Chloride is simultaneously analyzed with sodium, potassium, and silica.

CHLORIDE, Filtered
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	30	70	99 ± 15	99 ± 10	39 ± 6	39 ± 4	1	3
1983	30	70	101 ± 4	101 ± 3	40 ± 2	40 ± 2	1	1
1984	30	70	101 ± 9	101 ± 6	39 ± 10	39 ± 7	2	2
1985	25	75	102 ± 5	102 ± 3	50 ± 3	50 ± 2	1	1
1986	25	75	101 ± 3	101 ± 2	50 ± 2	50 ± 1	1	1

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	246	60	32	0.12	0.2	0.47	2.7	0.6	0.66	0.4
1983	200	44	21	0.25	0.19	0.27	3.9	0.6	0.42	0.6
1984	186	79	31	0.13	0.19	0.36	2.12	0.59	0.54	0.4
1985	198	39	31	0.21	0.33	0.78	3.48	0.97	1.27	0.6
1986	245	55	44	0.33	0.33	0.40	15.1	1.1	0.63	1

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	20.5	19.0	93
	70.2	68.0	97
1983	20.5	21.0	102
	70.2	70.5	100
1984	70.2	70.8	101
1985	70.2	70.0	100
1986	105.5	105.0	100
	193.3	190.0	98

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; field preserve with 5 mL of 50% HNO_3 acid (blue dot ampoule).

SAMPLE PREPARATION: A 50 mL aliquot of unfiltered sample is manually digested in a Kjeldahl flask with a mixture of HNO_3 and HCl acids at low heat and evaporated almost to dryness. After cooling, add 10 mL of 10% HCl to dissolve any residue. The sample is transferred to a culture tube for centrifugation to remove suspended materials.

ANALYTICAL PROCEDURE: Automated atomic emission spectrometry by direct aspiration into a high temperature (approximately 6500°K) argon plasma.

INSTRUMENTATION: A JARRELL-ASH (975 PLASMA ATOMCOMP) simultaneous multielement (26 channels) Inductively Coupled Argon Plasma Atomic Emission Spectrometer (ICAP-AES) with PDP-8 microprocessor and Digital Decwriter II printer.

SPECTRAL LINE: 267.7 nm

ANALYTICAL RANGE: 0-0.5 mg/L Cr LOWEST REPORTED VALUE: <0.001 mg/L Cr

CALIBRATION: 1 standard RESULTS REPORTED TO NEAREST: 0.001 mg/L Cr

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.400	0.100	0.492±0.057	0.492±0.038	0.297±0.060	0.297±0.040

WITHIN-RUN STD DEVIATION: 0.014 BETWEEN-RUN STD DEVIATION: 0.014

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	88	4	-
STANDARD DEVIATION	0.0015	0.0023	-
PRECISION (% RSD)	23.5	1.6	-

DETECTION LIMIT: 0.004 mg/L Cr

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.050	0.053	106
0.100	0.097	97
0.200	0.196	98

COMMENTS: All ICAP heavy metal parameters, with the exception of boron, are determined simultaneously in a single aliquot of sample.

CHROMIUM, Total
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	0.020	0.800	0.807 ±0.307	0.807 ±0.205	0.765±0.307	0.765 ±0.205	0.072	0.072
1984	0.800	0.020	0.820 ±0.049	0.820 ±0.033	0.781±0.048	0.781 ±0.032	0.011	0.011
1985	0.800	0.020	0.820 ±0.068	0.820 ±0.045	0.778±1.065	0.778 ±0.043	0.016	0.016
1986	0.400	0.100	0.489 ±0.026	0.489 ±0.018	0.294±0.021	0.294 ±0.014	0.005	0.006

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	LIMIT, mg/L
1982	-	-	-	-	-	-	-	-	-	-
1983	74	7	1	0.0011	0.0080	0.0290	12.6	9.4	5.9	0.003
1984	102	2	4	0.0019	0.0017	0.0039	20.4	9.4	1.3	0.006
1985	115	4	3	0.0017	0.0026	0.0064	16.4	1.8	1.80	0.005
1986	77	-	-	0.0030	-	-	20.7	-	-	0.009

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
	0.0070	0.0065	93
1982	0.060	0.056	93
	0.217	0.218	100
	0.010	0.0095	95
1983	0.080	0.077	96
	0.250	0.246	99
	0.080	0.075	94
1984	0.250	0.258	103
	0.050	0.051	102
1985	0.054	0.058	107
	0.012	0.013	108
	0.131	0.133	101
1986	0.261	0.257	99
	0.522	0.516	99

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; field preserve with 5 mL of 50% HNO_3 acid (blue dot ampoule).

SAMPLE PREPARATION: A 50 mL aliquot of unfiltered sample is manually digested in Kjeldahl flasks with a mixture of HNO_3 and HCl acids at low heat and evaporated almost to dryness. After cooling, add 10 mL of 10% HCl to dissolve any residue. The sample is transferred to a culture tube for centrifugation to remove suspended materials.

ANALYTICAL PROCEDURE: Automated atomic emission spectrometry by direct aspiration into a high temperature (approximately 6500°K) argon plasma.

INSTRUMENTATION: A JARRELL-ASH (975 PLASMA ATOMCOMP) simultaneous multielement (26 channels) Inductively Coupled Argon Plasma Atomic Emission Spectrometer (ICAP-AES) with PDP-8 microprocessor and Digital Decwriter II printer.

SPECTRAL LINE: 228.6 nm

ANALYTICAL RANGE: 0-0.5 mg/L Co LOWEST REPORTED VALUE: <0.001 mg/L Co

CALIBRATION: 1 standard RESULTS REPORTED TO NEAREST: 0.001 mg/L Co

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.400	0.100	0.509±0.030	0.509±0.020	0.307±0.028	0.307±0.019

WITHIN-RUN STD DEVIATION: 0.006 BETWEEN-RUN STD DEVIATION: 0.007

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	51	2	1
STANDARD DEVIATION	0.0011	0.0004	0.018
PRECISION (% RSD)	14.4	0.14	3.8

DETECTION LIMIT: 0.003 mg/L Co

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.05	0.049	98
0.10	0.098	98
0.20	0.192	96

COMMENTS: All ICAP heavy metal parameters, with the exception of boron, are determined simultaneously in a single aliquot of sample.

COBALT, Total

QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER						STD. DEVIATION	
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	WITHIN RUN	BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	0.800	0.020	0.829 ±0.094	0.829 ±0.063	0.789±0.090	0.789 ±0.060	0.021	0.022
1984	0.800	0.020	0.822 ±0.025	0.822 ±0.016	0.783±0.023	0.783 ±0.015	0.006	0.006
1985	0.800	0.020	0.825 ±0.064	0.825 ±0.043	0.784±1.059	0.784 ±0.039	0.014	0.015
1986	0.400	0.100	0.504 ±0.027	0.504 ±0.018	0.303±0.024	0.303 ±0.016	0.006	0.006

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	LIMIT, mg/L
1982	-	-	-	-	-	-	-	-	-	-
1983	27	4	-	0.0009	0.0093	-	12.2	2.6	-	0.003
1984	27	4	-	0.0008	0.0024	-	15.2	1.3	-	0.002
1985	49	-	-	0.0009	-	-	16.5	-	-	0.003
1986	56	-	-	0.0020	-	-	25.7	-	-	0.006

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	0.01	0.009	90
	0.50	0.473	95
	1.00	0.992	99
1983	0.02	0.018	90
	0.08	0.077	96
	0.60	0.586	98
1984	0.08	0.074	92
	0.60	0.60	100
1985	0.011	0.010	91
	0.12	0.119	99
	0.234	0.218	93
1986	0.131	0.130	99
	0.261	0.252	97
	0.522	0.508	97

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; field preserve with 5 mL of 50% HNO_3 acid (blue dot ampoule).

SAMPLE PREPARATION: A 50 mL aliquot of unfiltered sample is manually digested in a Kjeldahl flask with a mixture of HNO_3 and HCl acids at low heat and evaporated almost to dryness. After cooling, add 10 mL of 10% HCl to dissolve any residue. The sample is transferred to a culture tube for centrifugation to remove suspended materials.

ANALYTICAL PROCEDURE: Automated atomic emission spectrometry by direct aspiration into a high temperature (approximately 6500°K) argon plasma.

INSTRUMENTATION: A JARRELL-ASH (975 PLASMA ATOMCOMP) simultaneous multielement (26 channels) Inductively Coupled Argon Plasma Atomic Emission Spectrometer (ICAP-AES) with PDP-8 microprocessor and Digital Decwriter printer.

SPECTRAL LINE: 324.7 nm

ANALYTICAL RANGE: 0-0.5 mg/L Cu LOWEST REPORTED VALUE: <0.001 mg/L Cu

CALIBRATION: 1 standard RESULTS REPORTED TO NEAREST: 0.001 mg/L Cu

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.400	0.100	0.495±0.050	0.495±0.034	0.296±0.044	0.296±0.029

WITHIN-RUN STD DEVIATION: 0.011 BETWEEN-RUN STD DEVIATION: 0.011

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	82	6	6
STANDARD DEVIATION	0.0013	0.0034	0.0166
PRECISION (% RSD)	14.5	1.7	4.7

DETECTION LIMIT: 0.004 mg/L Cu

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.050	0.048	96
0.100	0.099	99
0.200	0.184	92

COMMENTS: All ICAP heavy metal parameters, with the exception of boron, are determined simultaneously in a single aliquot of sample.

COPPER, Total
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	0.020	0.800	0.817 ±0.098	0.817 ±0.065	0.778±0.094	0.778 ±0.063	0.022	0.023
1984	0.800	0.020	0.815 ±0.026	0.815 ±0.017	0.778±0.022	0.778 ±0.015	0.005	0.006
1985	0.800	0.020	0.820 ±0.084	0.820 ±0.056	0.779±0.083	0.779 ±0.055	0.020	0.020
1986	0.400	0.100	0.505 ±0.058	0.505 ±0.039	0.305±0.069	0.305 ±0.046	0.015	0.015

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	-	-	-	-	-	-	-	-	-	-
1983	110	9	3	0.0029	0.0073	0.0065	19.2	4.9	1.8	0.008
1984	126	1	3	0.0014	0.001	0.001	13.1	1.1	4.9	0.004
1985	102	7	2	0.0017	0.0051	0.019	14.2	4.2	5.9	0.005
1986	90	6	5	0.002	0.006	0.005	14.0	4.8	1.6	0.006

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	0.040	0.037	92
	0.250	0.238	95
	1.000	0.957	96
1983	0.050	0.047	94
	0.350	0.336	96
1984	0.050	0.045	90
	0.350	0.344	98
1985	0.012	0.012	100
	0.070	0.068	97
1986	0.170	0.168	99
	0.339	0.339	100
	0.678	0.658	97

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; field preserve with 5 mL of 6N NaOH (red dot ampoule).

SAMPLE PREPARATION: Unfiltered sample is mixed prior to pouring an aliquot for analysis.

ANALYTICAL PROCEDURE: In the automated distillation procedure, pyridine-barbituric acid colorimetric method, an aliquot of sample is mixed with phosphoric acid and flash distilled at 155°C into a phosphate buffer solution. The cyanogens are mixed with a pyridine-barbituric acid mixture to produce a red colored complex.

INSTRUMENTATION: A Technicon AutoAnalyzer II system with a 50 mm flowcell measures the absorbance of the red colored complex at 570 nm. A stripchart recorder displays the peaks.

ANALYTICAL RANGE: 0.002-0.100 mg/L CN LOWEST REPORTED VALUE: <0.002 mg/L CN

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 0.001 mg/L CN

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.075	0.025	0.101±0.004	0.101±0.003	0.051±0.003	0.051±0.002

WITHIN-RUN STD DEVIATION: 0.001 BETWEEN-RUN STD DEVIATION: 0.001

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	35	28	15
STANDARD DEVIATION	0.001	0.002	0.001
PRECISION (% RSD)	8.3	5.6	1.8

DETECTION LIMIT: 0.002 mg/L CN

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.500	0.480	96
0.500	0.517	103

COMMENTS: Only simple cyanides are measured by this procedure. Colorimetric reagent change from pyridine-pyrazolone to pyridine-barbituric acid implemented in 1978.

CYANIDE, Simple Extractable
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	0.075	0.025	0.101 ± 0.003	0.101 ± 0.002	0.050 ± 0.003	0.050 ± 0.002	0.0007	0.001
1983	0.075	0.025	0.100 ± 0.005	0.100 ± 0.003	0.050 ± 0.004	0.050 ± 0.002	0.0007	0.001
1984	0.075	0.025	0.100 ± 0.004	0.100 ± 0.003	0.050 ± 0.004	0.050 ± 0.002	0.0007	0.001
1985	0.075	0.025	0.101 ± 0.004	0.101 ± 0.003	0.050 ± 0.003	0.050 ± 0.002	0.0007	0.001
1986	0.075	0.025	0.099 ± 0.006	0.099 ± 0.004	0.051 ± 0.004	0.051 ± 0.003	0.0007	0.001

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	LIMIT, mg/L
1982	12	4	-	4.7×10^{-4}	0.001	-	6.5	3.1	-	0.001
1983	23	9	-	8.6×10^{-4}	8.6×10^{-4}	1.1×10^{-3}	16.2	4.3	1.5	0.002
1984	30	7	1	1.1×10^{-3}	1.5×10^{-3}	7.1×10^{-4}	19.9	5.8	1.3	0.003
1985	20	10	4	7.9×10^{-4}	7.8×10^{-4}	1.4×10^{-3}	9.0	2.5	1.9	0.002
1986	23	12	-	8.7×10^{-4}	1.2×10^{-3}	-	8.6	3.9	-	0.002

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	-	-	-
1983	0.020	0.0195	98
	0.100	0.100	100
1984	0.0129	0.0130	101
	0.0330	0.0320	97
	0.0516	0.0520	101
1985	0.080	0.083	104
	0.140	0.148	106
1986	-	-	-

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; no preservatives are added.

SAMPLE PREPARATION: An aliquot of sample is filtered through 0.45 micron membrane filter paper at the laboratory.

ANALYTICAL PROCEDURE: In the automated specific ion electrode method, an aliquot of sample is mixed with a CDTA buffer to prevent interferences and to adjust the pH of all samples and standards to a uniform value.

INSTRUMENTATION: A Technicon AutoAnalyzer II system with a fluoride specific ion electrode (lanthanum fluoride crystal) measures the fluoride ion activity using a flow-through cell and a calomel reference electrode. A stripchart recorder displays the sample peaks.

ANALYTICAL RANGE: 0.05-2.0 mg/L F LOWEST REPORTED VALUE: <0.05 mg/L F

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 0.01 mg/L F

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.50	1.50	2.02±0.10	2.02±0.07	1.02±0.09	1.02±0.06

WITHIN-RUN STD DEVIATION: 0.02 BETWEEN-RUN STD DEVIATION: 0.02

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	200	71	50
STANDARD DEVIATION	0.006	0.010	0.022
PRECISION (% RSD)	3.7	1.4	1.6

DETECTION LIMIT: 0.02 mg/L F

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1.00	1.00	100
2.00	1.93	96

COMMENTS: Fluoride is simultaneously analyzed with NO_2, NO_2 + NO_3, and sulfate.

FLUORIDE, Filtered
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	0.50	1.50	2.00 ± 0.16	2.00 ± 0.11	0.99 ± 0.10	0.99 ± 0.07	0.02	0.03
1983	0.50	1.50	2.05 ± 0.26	2.05 ± 0.17	1.01 ± 0.17	1.01 ± 0.11	0.04	0.05
1984	0.50	1.50	2.03 ± 0.16	2.03 ± 0.10	1.03 ± 0.08	1.03 ± 0.05	0.02	0.03
1985	0.50	1.50	2.03 ± 0.10	2.03 ± 0.07	1.01 ± 0.08	1.01 ± 0.05	0.02	0.02
1986	0.50	1.50	2.00 ± 0.14	2.00 ± 0.09	1.00 ± 0.10	1.00 ± 0.06	0.02	0.03

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	356	120	41	0.0085	0.008	0.011	2.6	1.2	0.79	0.03
1983	230	103	27	0.0118	0.024	0.046	6.6	4.0	3.3	0.04
1984	334	93	48	0.013	0.018	0.026	5.3	2.7	1.8	0.04
1985	305	107	49	0.005	0.012	0.02	3.4	1.8	1.8	0.02
1986	251	95	-	0.0057	0.018	0.027	4.5	2.6	2.0	0.02

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
	1.7	1.6	94
1982	0.63	0.65	103
	1.7	1.7	100
1983	1.18	1.10	93
	0.08	0.09	112
1984	0.26	0.26	100
	0.56	0.57	102
1985	1.30	1.28	98
	1.77	1.66	94
	0.43	0.43	100
1986	0.051	0.50	98

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; no preservatives are added to the routine parameter bottle.

SAMPLE PREPARATION: A 10 mL aliquot of unfiltered, mixed sample is acidified with 0.5 mL of 50% HNO_3 at least 2 hours prior to analysis.

ANALYTICAL PROCEDURE: In this direct aspiration atomic absorption method, acidified samples are aspirated directly into an air-acetylene flame.

INSTRUMENTATION: A Hitachi 180-80 Polarized Zeeman atomic absorption spectrophotometer measures the absorbance at 248.3 nm. A stripchart recorder displays the sample peaks.

ANALYTICAL RANGE: 0.05-6.0 mg/L Fe LOWEST REPORTED VALUE: <0.05 mg/L Fe

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 0.01 mg/L Fe

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.50	1.50	1.98±0.08	1.98±0.05	1.00±0.05	1.00±0.03

WITHIN-RUN STD DEVIATION: 0.01 BETWEEN-RUN STD DEVIATION: 0.02

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	128	41	19
STANDARD DEVIATION	0.008	0.012	0.011
PRECISION (% RSD)	18.3	2.1	0.8

DETECTION LIMIT: 0.02 mg/L Fe

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.084	0.09	107
0.84	0.82	98

COMMENTS: Iron results from unpreserved samples represent minimal iron values since iron oxides irreversibly deposit onto the sample container walls.

IRON, Acid Extractable
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER						STD. DEVIATION	
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	WITHIN RUN	BETWEEN RUN
1982	0.25	1.50	1.74 ± 0.11	1.74 ± 0.07	1.23 ±0.10	1.23 ± 0.07	0.02	0.03
1983	0.25	1.50	1.77 ± 0.12	1.77 ± 0.08	1.26 ±0.08	1.26 ± 0.05	0.02	0.02
1984	0.25	1.50	1.74 ± 0.05	1.74 ± 0.03	1.26 ±0.05	1.26 ± 0.04	0.01	0.01
1985	0.50	1.50	2.00 ± 0.15	2.00 ± 0.10	1.00 ±0.13	1.00 ± 0.09	0.03	0.12
1986	0.50	1.50	2.00 ± 0.07	2.00 ± 0.05	1.00 ±0.06	1.00 ± 0.04	0.01	0.02

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	111	53	51	0.019	0.022	0.032	16.3	3.2	2.2	0.06
1983	104	32	33	0.007	0.011	0.018	7.64	1.8	1.3	0.02
1984	34	7	4	0.009	0.026	0.014	11.1	3.7	0.91	0.03
1985	138	43	16	0.014	0.049	0.14	6.41	2.5	3.1	0.04
1986	324	65	31	0.008	0.013	0.039	4.3	1.1	1.4	0.02

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
	0.67	0.66	98
1982	1.33	1.48	111
	0.30	0.33	110
1983	0.31	0.32	103
	0.51	0.49	96
1984	1.07	0.99	92
	1.12	1.15	103
1985	2.00	1.96	98
	0.22	0.22	100
1986	0.50	0.49	98

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; field preserve with 5 mL of 50% HNO_3 (blue dot ampoule).

SAMPLE PREPARATION: The pH of a 100 mL aliquot of unfiltered sample is adjusted to pH 4.8 (mixed methyl red-bromphenol blue indicator) using dilute H_2SO_4 in a 250 mL volumetric flask.

ANALYTICAL PROCEDURE: Add 5 mL of an acetate buffer (pH 3.4) and 5 mL of 2% APDC. After 5 minutes, add 8 mL of MIBK and mix for 10 minutes. Add distilled water to float MIBK into the neck of the flask.

INSTRUMENTATION: A Perkin-Elmer 603 atomic absorption spectrophotometer measures the absorbance at 283.5 nm. A stripchart recorder displays the sample peaks.

ANALYTICAL RANGE: 0.003-0.200 mg/L Pb LOWEST REPORTED VALUE: <0.003 mg/L Pb

CALIBRATION: 6 standards RESULTS REPORTED TO NEAREST: 0.001 mg/L Pb

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.150	0.050	0.205 ± 0.033	0.205 ± 0.022	0.101 ± 0.019	0.101 ± 0.012

WITHIN-RUN STD DEVIATION: 0.004 BETWEEN-RUN STD DEVIATION: 0.006

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	23	5	3
STANDARD DEVIATION	0.001	0.001	0.003
PRECISION (% RSD)	16.8	2.0	1.9

DETECTION LIMIT: 0.003 mg/L Pb

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.026	0.027	104
0.050	0.045	90
0.100	0.102	102

COMMENTS:

LEAD, Extractable
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	0.020	0.100	0.118±0.023	0.118±0.015	0.080±0.022	0.080±0.014	0.005	0.005
1984	0.100	0.300	0.405±0.045	0.405±0.030	0.198±0.039	0.198±0.026	0.009	0.010
1985	0.300	0.100	0.400±0.048	0.400±0.032	0.200±0.034	0.200±0.023	0.008	0.010
1986	0.300	0.100	0.402±0.037	0.402±0.024	0.197±0.024	0.197±0.016	0.006	0.007

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	9	5	2	0.0015	0.0025	0.0092	13.8	1.7	3.8	0.004
1983	64	6	1	0.0012	0.0048	0.0014	13.8	3.3	0.5	0.004
1984	41	6	4	0.0013	0.0016	0.0064	18.2	1.1	2.4	0.004
1985	50	7	3	0.0011	0.0019	0.097	8.0	2.2	11.5	0.003
1986	21	1	1	0.0022	0.0014	0.0028	14.4	1.8	1.4	0.006

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	0.080	0.082	102
	0.348	0.348	100
1983	0.007	0.008	114
	0.024	0.022	92
1984	0.006	0.006	100
	0.504	0.505	100
1985	0.074	0.071	96
	1.54	1.48	96
1986	0.021	0.020	95
	0.043	0.044	102

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; field preservatives are not added.

SAMPLE PREPARATION: At the laboratory, a 10 mL aliquot of filtered sample is acidified with 0.5 mL of 50% HNO_3.

ANALYTICAL PROCEDURE: Automated atomic absorption method in which an aliquot of acidified sample is mixed with lanthanum chloride solution and aspirated into an air acetylene flame.

INSTRUMENTATION: The absorbance of magnesium is measured at 285.2 nm using a IL 251 atomic absorption spectrophotometer. A stripchart recorder displays the peaks.

ANALYTICAL RANGE: 1-100 mg/L Mg LOWEST REPORTED VALUE: <1 mg/L Mg

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 1 mg/L Mg

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
25	75	98 ± 6	98 ± 4	49 ± 4	49 ± 3

WITHIN-RUN STD DEVIATION: 0.7 BETWEEN-RUN STD DEVIATION: 1

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	147	61	19
STANDARD DEVIATION	0.4	0.7	1.1
PRECISION (% RSD)	19.2	2.4	1.4

DETECTION LIMIT: 1 mg/L Mg

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
5.0	4.8	96
10.0	10.2	102

COMMENTS: Magnesium is analyzed from the same sample aliquot analyzed for calcium. Acidification of sample aliquot was implemented on August 15, 1985.

MAGNESIUM, Acid Extractable
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	20	75	91 ± 8	91 ± 5	53 ± 5	53 ± 4	1	2
1983	25	75	96 ± 5	96 ± 3	48 ± 5	48 ± 4	1	1
1984	24	75	96 ± 5	96 ± 3	48 ± 4	48 ± 2	1	1
1985	25	75	97 ± 12	97 ± 8	48 ± 12	48 ± 8	3	3
1986	25	75	97 ± 6	97 ± 4	49 ± 5	49 ± 3	1	1

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	183	112	44	0.55	0.86	1.6	6.8	2.9	2.2	2
1983	174	77	27	0.59	0.77	2.8	5.2	2.4	5.9	2
1984	106	67	21	0.49	0.64	1.4	5.7	2.0	2.2	1
1985	137	72	18	0.53	0.75	1.6	5.7	2.5	2.2	2
1986	186	138	32	0.46	0.88	1.8	5.1	2.9	2.5	1

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	7.1	6.0	84
1983	7.1	6.0	84
1984	7.5	7.5	100
	9.5	9.6	101
	30.9	31.0	100
1985	8.4	9.0	107
1986	9.4	10.0	106
	21.3	22.0	103

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; field preserve with 5 mL of 50% HNO_3 acid (blue dot ampoule).

SAMPLE PREPARATION: A 50 mL aliquot of unfiltered sample is manually digested in Kjeldahl flasks with a mixture of HNO_3 and HCl acids at low heat and evaporated almost to dryness. After cooling, add 10 mL of 10% HCl to dissolve any residue. The sample is transferred to a culture tube for centrifugation to remove suspended materials.

ANALYTICAL PROCEDURE: Automated atomic emission spectrometry by direct aspiration into a high temperature (approximately 6500°K) argon plasma.

INSTRUMENTATION: A JARRELL-ASH (975 PLASMA ATOMCOMP) simultaneous multielement (26 channels) Inductively Coupled Argon Plasma Atomic Emission Spectrometer (ICAP-AES) with PDP-8 microprocessor and Digital Decwriter II printer.

SPECTRAL LINE: 257.6 nm

ANALYTICAL RANGE: 0-0.5 mg/L Mn LOWEST REPORTED VALUE: <0.001 mg/L Mn

CALIBRATION: 1 standard RESULTS REPORTED TO NEAREST: 0.001 mg/L Mn

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.400	0.100	0.501±0.027	0.501±0.018	0.303±0.025	0.303±0.017

WITHIN-RUN STD DEVIATION: 0.004 BETWEEN-RUN STD DEVIATION: 0.006

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	73	10	8
STANDARD DEVIATION	0.0012	0.0056	0.0105
PRECISION (% RSD)	13.0	4.1	2.6

DETECTION LIMIT: 0.004 mg/L Mn

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.05	0.046	92
0.10	0.978	98
0.20	0.188	94

COMMENTS: All ICAP heavy metal parameters, with the exception of boron, are determined simultaneously in a single aliquot of sample.

MANGANESE, Total
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	0.800	0.020	0.822 ±0.093	0.822 ±0.062	0.782±0.091	0.782 ±0.060	0.021	0.022
1984	0.800	0.020	0.820 ±0.021	0.820 ±0.014	0.783±0.019	0.783 ±0.013	0.004	0.005
1985	0.800	0.020	0.826 ±0.073	0.826 ±0.049	0.785±1.070	0.785 ±0.046	0.016	0.017
1986	0.400	0.100	0.499 ±0.029	0.499 ±0.020	0.301±0.023	0.301 ±0.016	0.006	0.006

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	LIMIT, mg/L
1982	-	-	-	-	-	-	-	-	-	-
1983	97	18	12	0.0016	0.0037	0.0095	6.1	2.1	2.6	0.004
1984	91	34	15	0.0011	0.0039	0.0082	6.9	2.2	2.6	0.003
1985	78	25	20	0.0019	0.0073	0.0171	9.3	4.1	5.4	0.006
1986	41	13	19	0.0023	0.0087	0.0147	8.5	6.4	4.1	0.006

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	0.055	0.050	91
	0.350	0.348	99
1983	0.015	0.014	93
	0.075	0.069	92
	0.500	0.476	95
1984	0.075	0.067	89
	0.500	0.492	98
1985	0.045	0.045	100
	0.100	0.095	95
1986	0.174	0.170	98
	0.348	0.335	96
	0.696	0.681	98

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect 125 mL of sample in a polypropylene sample container; field preserve with 2 mL of a dichromate-nitric acid mixture (yellow dot ampoule).

SAMPLE PREPARATION: Unfiltered sample is mixed prior to pouring an aliquot for analysis.

ANALYTICAL PROCEDURE: In the automated cold vapour method, organic and inorganic mercury compounds are oxidized with sulfuric acid and potassium persulfate in an automated heating bath (100°C) followed by a reduction to elemental mercury using stannous chloride.

INSTRUMENTATION: Nitrogen gas is utilized to sparge the elemental mercury vapour into a Pharmacia UV Mercury Monitor where the absorption is measured at 253.7 nm. A stripchart recorder is used to display the peaks.

ANALYTICAL RANGE: 0.0001-0.0025 mg/L Hg LOWEST REPORTED VALUE: <0.0001 mg/L H

CALIBRATION: 7 standards RESULTS REPORTED TO NEAREST: 0.0001 mg/L H

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A+B)}$ LIMITS		$\overline{(A-B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.0020	0.0005	0.0025 ± 0.0003	0.0025 ± 0.0002	0.0014 ± 0.0002	0.0014 ± 0.0002

WITHIN-RUN STD DEVIATION: 0.00006 BETWEEN-RUN STD DEVIATION: 0.00007

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	16	6	7
STANDARD DEVIATION	0.00004	0.00009	0.00007
PRECISION (% RSD)	30.0	13.0	3.6

DETECTION LIMIT: 0.0001 mg/L Hg

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.00180	0.00178	99
0.00360	0.00350	97

COMMENTS: Presence of chlorine would result in a spectral interference with a positive bias.

MERCURY, Total
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	0.0005	0.0020	0.0025 ±0.0003	0.0025 ±0.0002	0.0015 ±0.0002	0.0015 ±0.0002	0.00006	0.00006
1983	0.0020	0.0005	0.0024 ±0.0004	0.0024 ±0.0003	0.0015 ±0.0003	0.0015 ±0.0002	0.00007	0.00008
1984	0.0020	0.0005	0.0024 ±0.0007	0.0024 ±0.0004	0.0014 ±0.0005	0.0014 ±0.0003	0.0001	0.0002
1985	0.0020	0.0005	0.0025 ±0.0002	0.0025 ±0.0001	0.0015 ±0.0002	0.0015 ±0.0002	0.00007	0.0001
1986	0.0020	0.0005	0.0025 ±0.0003	0.0025 ±0.0002	0.0014 ±0.0003	0.0014 ±0.0002	0.00006	0.00007

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	LIMIT, mg/L
1982	-	-	-	-	-	-	-	-	-	-
1983	18	7	-	2.5×10^{-4}	8.38×10^{-4}	-	7.8	11.4	-	0.0008
1984	14	10	12	1.3×10^{-4}	6.8×10^{-5}	1.8×10^{-4}	5.5	2.3	3.7	0.0004
1985	2	1	11	7.0×10^{-5}	7.0×10^{-5}	5.3×10^{-4}	33.6	8.3	8.2	0.0002
1986	4	4	-	1.4×10^{-4}	2.6×10^{-4}	-	13.6	8.6	-	0.0004

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
	0.00300	0.00290	97
1982	0.00067	0.00065	97
	0.00750	0.00750	100
	0.00175	0.00186	106
1983	0.00350	0.00350	100
1984	0.00200	0.00200	100
	0.00200	0.00200	100
1985	0.00437	0.00430	98
	0.00175	0.00177	101
1986	0.0036	0.0036	100

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; field preserve with 5 mL of 50% HNO_3 acid (blue dot ampoule).

SAMPLE PREPARATION: A 50 mL aliquot of unfiltered sample is manually digested in Kjeldahl flasks with a mixture of HNO_3 and HCl acids at low heat and evaporated almost to dryness. After cooling, add 10 mL of 10% HCl to dissolve any residue. The sample is transferred to a culture tube for centrifugation to remove suspended materials.

ANALYTICAL PROCEDURE: Automated atomic emission spectrometry by direct aspiration into a high temperature (approximately 6500°K) argon plasma.

INSTRUMENTATION: A JARRELL-ASH (975 PLASMA ATOMCOMP) simultaneous multielement (26 channels) Inductively Coupled Argon Plasma Atomic Emission Spectrometer (ICAP-AES) with PDP-8 microprocessor and Digital Decwriter II printer.

SPECTRAL LINE: 202.0 nm

ANALYTICAL RANGE: 0-0.5 mg/L Mo LOWEST REPORTED VALUE: <0.001 mg/L Mo

CALIBRATION: 1 standard RESULTS REPORTED TO NEAREST: 0.001 mg/L Mo

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.400	0.100	0.498±0.042	0.498±0.028	0.304±0.042	0.304±0.028

WITHIN-RUN STD DEVIATION: 0.010 BETWEEN-RUN STD DEVIATION: 0.010

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	44	7	-
STANDARD DEVIATION	0.0013	0.0089	-
PRECISION (% RSD)	24.0	4.6	-

DETECTION LIMIT: 0.0039 mg/L Mo

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.897	0.827	92
1.68	1.59	95

COMMENTS: All ICAP heavy metal parameters, with the exception of boron, are determined simultaneously in a single aliquot of sample.

MOLYBDENUM, Total
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	0.800	0.020	0.815 ±0.100	0.815 ±0.067	0.779±0.095	0.779 ±0.063	0.023	0.023
1984	0.800	0.020	0.824 ±0.091	0.824 ±0.061	0.786±0.083	0.786 ±0.056	0.020	0.021
1985	0.800	0.020	0.834 ±0.102	0.834 ±0.068	0.782±1.099	0.782 ±0.066	0.023	0.024
1986	0.400	0.100	0.498 ±0.031	0.498 ±0.020	0.302±0.026	0.302 ±0.017	0.006	0.007

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	-	-	-	-	-	-	-	-	-	-
1983	29	3	1	0.0018	0.0038	0.0042	11.1	3.0	1.0	0.005
1984	47	5	3	0.0019	0.0017	0.010	12.7	1.4	3.1	0.006
1985	44	20	3	0.0017	0.0066	0.011	12.4	4.3	4.2	0.005
1986	12	13	-	0.002	0.006	-	15.5	4.1	-	0.006

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	1.50	1.40	93
1983	0.008	0.009	112
	0.484	0.463	96
1984	0.84	0.89	106
	4.64	4.25	92
1985	0.012	0.012	100
	0.946	0.911	96
1986	0.015	0.014	93
	0.070	0.075	107
	0.905	0.982	108

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; field preserve with 5 mL of 50% HNO_3 acid (blue dot ampoule).

SAMPLE PREPARATION: A 50 mL aliquot of unfiltered sample is manually digested in a Kjeldahl flask with a mixture of HNO_3 and HCl acids at low heat and evaporated almost to dryness. After cooling, add 10 mL of 10% HCl to dissolve any residue. The sample is transferred to a culture tube for centrifugation to remove suspended materials.

ANALYTICAL PROCEDURE: Automated atomic emission spectrometry by direct aspiration into a high temperature (approximately 6500°K) argon plasma.

INSTRUMENTATION: A JARRELL-ASH (975 PLASMA ATOMCOMP) simultaneous multielement (26 channels) Inductively Coupled Argon Plasma Atomic Emission Spectrometer (ICAP-AES) with PDP-8 microprocessor and Digital Decwriter II printer.

SPECTRAL LINE: 231.6 nm

ANALYTICAL RANGE: 0.001-0.5 mg/L Ni LOWEST REPORTED VALUE: <0.001 mg/L Ni

CALIBRATION: 1 standard RESULTS REPORTED TO NEAREST: 0.001 mg/L Ni

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.400	0.100	0.503±0.031	0.0503±0.021	0.0304±0.028	0.304±0.018

WITHIN-RUN STD DEVIATION: 0.006 BETWEEN-RUN STD DEVIATION: 0.007

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	85	4	1
STANDARD DEVIATION	0.0018	0.0028	0.0014
PRECISION (% RSD)	27.4	2.2	0.3

DETECTION LIMIT: 0.005 mg/L Ni

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.05	0.048	96
0.10	0.099	99
0.20	0.188	94

COMMENTS: All ICAP heavy metal parameters, with the exception of boron, are determined simultaneously in a single aliquot of sample.

NICKEL, Total
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)}\pm 3s$	WARNING LIMITS $\overline{(A+B)}\pm 2s$	CONTROL LIMITS $\overline{(A-B)}\pm 3s$	WARNING LIMITS $\overline{(A-B)}\pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	0.020	0.800	0.827 ± 0.095	0.827 ± 0.063	0.788 ± 0.090	0.788 ± 0.060	0.021	0.022
1984	0.800	0.020	0.820 ± 0.039	0.820 ± 0.026	0.782 ± 0.037	0.782 ± 0.025	0.008	0.009
1985	0.800	0.020	0.834 ± 0.065	0.834 ± 0.043	0.792 ± 0.060	0.792 ± 0.040	0.014	0.015
1986	0.400	0.100	0.497 ± 0.029	0.497 ± 0.019	0.299 ± 0.024	0.299 ± 0.016	0.006	0.006

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	-	-	-	-	-	-	-	-	-	-
1983	99	2	4	0.0027	0.0046	0.0039	22.8	2.4	1.0	0.008
1984	100	4	2	0.0023	0.0054	0.0049	22.0	3.0	1.6	0.006
1985	139	2	1	0.0016	0.0038	0.007	16.6	3.1	0.6	0.004
1986	88	2	2	0.003	0.002	0.003	16.6	1.2	1.1	0.009

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	0.070	0.061	87
	0.250	0.234	92
	0.340	0.319	94
1983	0.030	0.029	97
	0.080	0.077	96
	0.300	0.284	95
1984	0.080	0.071	89
	0.300	0.294	98
1985	0.060	0.057	95
	0.012	0.013	108
	0.276	0.249	90
1986	0.104	0.098	94
	0.207	0.194	94
	0.414	0.404	98

SAMPLE TYPE: Drinking Waters and Surface Waters.

SAMPLE PRESERVATION: Collect sample in a 125 mL polyethylene bottle; field preserve with 2 mL of 5% H_2SO_4 (brown dot ampoule).

SAMPLE PREPARATION: An in-line dialyzer separates ammonia nitrogen from particulates and interferences present in the sample.

ANALYTICAL PROCEDURE: In the automated alkaline phenol-hypochlorite (Berthelot reaction) colorimetric procedure, dialyzed ammonia is mixed with EDTA, alkaline phenate and sodium hypochlorite in the presence of nitroprusside catalyst to produce a blue coloured solution.

INSTRUMENTATION: A Technicon AutoAnalyzer II system with a 50 mm flow cell measures the absorbance of the blue colour at 630 nm. A stripchart recorder displays the sample peaks.

LOW RANGE

ANALYTICAL RANGE: 0.002-0.200 mg/L N LOWEST REPORTED VALUE: <0.002 mg/L N

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 0.001 mg/L N

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.125	0.030	0.153±0.020	0.153±0.013	0.095 ±0.016	0.095±0.011

WITHIN-RUN STD DEVIATION: 0.0035 BETWEEN-RUN STD DEVIATION: 0.004

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	48	21	10
STANDARD DEVIATION	0.002	0.004	0.003
PRECISION (% RSD)	13.8	6.7	2.1

DETECTION LIMIT: 0.006 mg/L N

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.100	0.103	103

COMMENTS: Ammonia gradually disappears from unpreserved samples. Chemical conversion to nitrites and nitrates also occurs. Excess preservative reduces the recovery of ammonia in the analysis.

NITROGEN-AMMONIA, Dissolved
Low Range
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)}\pm 3s$	WARNING LIMITS $\overline{(A+B)}\pm 2s$	CONTROL LIMITS $\overline{(A-B)}\pm 3s$	WARNING LIMITS $\overline{(A-B)}\pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	-	-	-	-	-	-	-	-
1984	0.125	0.030	0.162±0.061	0.162±0.041	0.092±0.063	0.092±0.042	0.015	0.015
1985	0.125	0.030	0.156±0.012	0.156±0.008	0.096±0.008	0.096±0.005	0.021	0.010
1986	0.125	0.030	0.152±0.027	0.152±0.018	0.093±0.022	0.093±0.015	0.005	0.006

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	-	-	-	-	-	-	-	-	-	-
1983	-	-	-	-	-	-	-	-	-	-
1984	49	10	11	0.0030	0.0084	0.0084	17.4	12.5	6.2	0.009
1985	55	24	16	0.0023	0.0043	0.0054	23.2	7.5	4.1	0.007
1986	42	11	13	0.0028	0.0039	0.0042	18.4	6.2	3.0	0.008

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	0.190	0.188	99
1983	-	-	-
1984	0.150	0.160	107
1985	0.019	0.022	116
	0.150	0.154	102
1986	0.004	0.004	100
	0.006	0.005	83

SAMPLE TYPE: Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 125 mL polyethylene bottle; field preserve with 2 mL of 5% H_2SO_4 (brown dot ampoule).

SAMPLE PREPARATION: An in-line dialyzer separates ammonia nitrogen from particulates and interferences present in the sample.

ANALYTICAL PROCEDURE: In the automated alkaline phenol-hypochlorite (Berthelot Reaction) colorimetric procedure, dialyzed ammonia is mixed with EDTA, alkaline phenate and sodium hypochlorite in the presence of nitroprusside catalyst to produce a blue coloured solution.

INSTRUMENTATION: A Technicon AutoAnalyzer II system with a 50 mm flow cell measures the absorbance of the blue colour at 630 nm. A stripchart recorder displays the sample peaks.

HIGH RANGE

ANALYTICAL RANGE: 0.05-2.0 mg/L N LOWEST REPORTED VALUE: <0.05 mg/L N

CALIBRATION: 6 standards RESULTS REPORTED TO NEAREST: 0.01 mg/L N

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
1.20	0.03	1.25 ± 0.087	1.25 ± 0.058	1.19 ± 0.083	1.19 ± 0.056

WITHIN-RUN STD DEVIATION: 0.02 BETWEEN-RUN STD DEVIATION: 0.02

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	82	9	6
STANDARD DEVIATION	0.005	0.014	0.021
PRECISION (% RSD)	12.0	2.2	1.6

DETECTION LIMIT: 0.02 mg/L N

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1.00	1.03	103
2.00	1.98	99

COMMENTS: Ammonia gradually disappears from unpreserved samples. Chemical conversion to nitrites and nitrates also occurs. Excess preservative reduces the recovery of ammonia in the analysis.

NITROGEN-AMMONIA, Dissolved
High Range

QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	1.50	0.50	2.00 ± 0.08	2.00 ± 0.05	1.96 ± 0.62	1.96 ± 0.41	0.02	0.02
1983	1.50	0.50	2.01 ± 0.14	2.01 ± 0.09	1.01 ± 0.08	1.01 ± 0.05	0.02	0.03
1984	1.50	0.50	2.01 ± 0.12	2.01 ± 0.08	1.01 ± 0.12	1.01 ± 0.08	0.03	0.03
1985	1.20	0.030	1.24 ± 0.047	1.24 ± 0.031	1.18 ± 0.047	1.18 ± 0.031	0.01	0.01
1986	1.20	0.030	1.25 ± 0.0039	1.25 ± 0.026	1.19 ± 0.044	1.19 ± 0.029	0.01	0.01

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	18	6	8	0.0034	0.0021	0.0016	5.5	0.36	0.11	0.010
1983	86	6	4	0.0033	0.025	0.024	3.2	1.8	1.8	0.010
1984	111	18	16	0.0041	0.010	0.021	9.8	1.7	1.4	0.012
1985	103	18	20	4.3×10^{-3}	0.0076	0.050	15.2	1.3	3.2	0.012
1986	76	13	12	0.0041	0.033	0.038	12.2	7.6	2.6	0.012

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
	0.19	0.188	99
1982	1.22	1.27	104
	0.194	0.016	84
1983	0.029	0.029	100
	0.150	0.140	93
1984	0.304	0.310	102
	1.52	1.55	102
	0.150	0.154	103
1985	0.019	0.022	116
	0.004	0.004	100
1986	1.52	1.54	101

SAMPLE TYPE: Drinking Waters, Surface Waters, Municipal, and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 125 mL polyethylene bottle; field preserve with 2 mL of 5% H_2SO_4 (brown dot ampoule).

SAMPLE PREPARATION: Unfiltered sample is mixed prior to withdrawing an aliquot for digestion with H_2SO_4, K_2SO_4, and HgO catalyst. A two stage heating cycle (200°C and 360°C) converts organic nitrogen to ammonium sulfate.

ANALYTICAL PROCEDURE: In the block digestion, automated phenol-hypochlorite (Berthelot reaction) colorimetric method, an aliquot of digested sample is mixed with EDTA, alkaline phenate and sodium hypochlorite in the presence of nitroprusside catalyst to produce a blue colored solution.

INSTRUMENTATION: A Technicon BD-40 Block Digestor and a Technicon AutoAnalyzer II system with a 50 mm flow cell measures the absorbance of the blue color at 630 nm. A stripchart recorder displays the sample peaks.

ANALYTICAL RANGE: 0.05-2.0 mg/L N LOWEST REPORTED VALUE: <0.02 mg/L N

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 0.01 mg/L N

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
1.50	0.50	2.00±0.089	2.00±0.059	0.99±0.069	0.99±0.046

WITHIN-RUN STD DEVIATION: 0.016 BETWEEN-RUN STD DEVIATION: 0.019

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	38	44	35
STANDARD DEVIATION	0.018	0.025	0.035
PRECISION (% RSD)	13.0	3.9	2.4

DETECTION LIMIT: 0.05 mg/L N

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
5.00	5.10	102
5.00	4.98	100

COMMENTS: Loss of ammonia will reduce TKN results. TKN is simultaneously analyzed with total phosphorus.

NITROGEN-KJELDAHL, Total
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	1.50	0.50	1.99±0.29	1.99±0.20	1.00±0.24	1.00±0.16	0.06	0.06
1983	1.50	0.50	2.00±0.06	2.00±0.04	1.00±0.04	1.00±0.03	0.01	0.01
1984	1.50	0.50	2.00±0.07	2.00±0.05	0.99±0.05	0.99±0.03	0.01	0.01
1985	1.50	0.50	2.00±0.08	2.00±0.05	0.99±0.05	0.99±0.04	0.01	0.02
1986	1.50	0.50	2.00±0.09	2.00±0.06	1.00±0.06	1.00±0.04	0.014	0.02

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	LIMIT, mg/L
1982	12	10	6	0.0041	0.0090	0.0070	1.5	1.4	0.5	0.01
1983	23	46	25	0.015	0.018	0.027	3.6	3.0	2.0	0.04
1984	116	96	56	0.018	0.023	0.016	9.6	3.6	1.2	0.05
1985	92	90	65	0.019	0.020	0.015	13.3	3.1	1.1	0.06
1986	50	75	51	0.022	0.023	0.027	14.0	3.7	1.9	0.07

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	0.52	0.50	96
	4.12	4.30	104
1983	-	-	-
1984	0.17	0.19	95
	0.40	0.40	100
	0.52	0.52	100
1985	0.48	0.49	104
	0.52	0.50	96
	3.84	3.90	102
1986	0.143	0.143	100
	0.400	0.430	107

SAMPLE TYPE: Rivers & Lakes (Surface Waters).

SAMPLE PRESERVATION: Collect sample in a 125 mL polyethylene bottle; no preservatives are added.

SAMPLE PREPARATION: Low level nitrate analyses are completed on a field filtered (0.45 micron pore size) sample.

ANALYTICAL PROCEDURE: In the automated diazotization colorimetric procedure, an aliquot of sample is mixed with a buffered EDTA solution before passing through a copper coated cadmium column to reduce nitrate to nitrite ions. Nitrite is diazotized with sulfonilamide and coupled with N-(1-naphthyl)ethylene diamine dihydrochloride to form a purple-red coloured dye.

INSTRUMENTATION: A Technicon AutoAnalyzer II system with a 50 mm flow cell measures the absorbance at 520 nm. A stripchart recorder displays the sample peaks.

LOW RANGE

ANALYTICAL RANGE: 0.001-0.200 mg/L N LOWEST REPORTED VALUE: <0.001 mg/L N

CALIBRATION: 6 standards RESULTS REPORTED TO NEAREST: 0.001 mg/L N

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.150	0.050	0.197±0.007	0.197±0.004	0.098 ±0.005	0.098±0.003

WITHIN-RUN STD DEVIATION: 0.001 BETWEEN-RUN STD DEVIATION: 0.001

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	32	22	13
STANDARD DEVIATION	0.0011	0.0028	0.0035
PRECISION (% RSD)	23.6	10.8	2.0

DETECTION LIMIT: 0.003 mg/L N

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
2.00	1.95	98
2.00	1.97	98

COMMENTS: Nitrate + nitrite nitrogen can increase due to conversion of ammonia. Biological or biochemical reduction to nitrogen gas can reduce the NO_2 + NO_3 level in natural samples.

NITROGEN-NITRATE+NITRITE, Filtered
Low Range

QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	0.060	0.020	0.080 ± 0.009	0.080±0.006	0.040 ±0.009	0.040 ±0.006	0.002	0.002
1983	0.060	0.020	0.080 ± 0.009	0.080±0.006	0.041 ±0.012	0.041 ±0.008	0.003	0.002
1984	0.060	0.020	0.082 ± 0.006	0.082±0.004	0.040 ±0.003	0.040 ±0.002	0.0007	0.001
1985	0.060	0.020	0.081 ± 0.003	0.081±0.002	0.041 ±0.002	0.041 ±0.001	0.0007	0.001
1986	0.060	0.020	0.081 ± 0.002	0.081±0.002	0.041 ±0.002	0.041 ±0.001	0.0007	0.001

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION
	0–20%	20–50%	50–100%	0–20%	20–50%	50–100%	0–20%	20–50%	50–100%	LIMIT, mg/L
1982	52	17	19	0.0002	0.001	0.002	5.4	3.3	1.8	0.001
1983	99	33	38	0.0007	0.0006	0.0009	4.2	2.0	0.74	0.002
1984	91	25	23	0.0003	0.0007	0.001	4.4	2.2	1.5	0.001
1985	57	17	48	0.0002	0.0005	0.001	5.4	1.5	1.3	0.001
1986	26	13	18	0.0004	0.0009	0.001	10.2	2.6	1.3	0.001

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	0.180	0.185	103
	1.288	1.285	100
	1.320	1.322	100
1983	0.535	0.600	112
	1.93	2.05	106
1984	0.18	0.19	106
	0.084	0.082	98
	1.61	1.649	102
1985	0.084	0.087	104
	0.180	0.165	92
1986	0.032	0.030	94
	0.570	0.600	105
	1.61	1.475	92

SAMPLE TYPE: Drinking Waters, Municipal, and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; no preservative is added.

SAMPLE PREPARATION: An aliquot of sample is filtered through a 0.45 micron membrane filter at the laboratory.

ANALYTICAL PROCEDURE: In the automated diazotization colorimetric procedure, an aliquot of sample is mixed with a buffered EDTA solution before passing through a copper coated cadmium column to reduce nitrate to nitrite ions. Nitrite is diazotized with sulfonilamide and coupled with N-(1-naphthyl)ethylene diamine dihydrochloride to form a purple-red coloured dye.

INSTRUMENTATION: A Technicon AutoAnalyzer II system with a 15 mm flow cell measures the absorbance at 520 nm. A stripchart recorder displays the sample peaks.

HIGH RANGE

ANALYTICAL RANGE: 0.01-2.0 mg/L N LOWEST REPORTED VALUE: <0.02 mg/L N

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 0.01 mg/L N

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.50	1.50	1.98±0.06	1.98±0.04	1.01 ±0.04	1.01±0.03

WITHIN-RUN STD DEVIATION: 0.007 BETWEEN-RUN STD DEVIATION: 0.010

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	111	29	16
STANDARD DEVIATION	0.002	0.005	0.007
PRECISION (% RSD)	9.9	0.8	0.5

DETECTION LIMIT: 0.006 mg/L N

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
2.00	2.02	101
0.58	0.60	103
0.34	0.35	103

COMMENTS: Nitrate + nitrite nitrogen can increase due to conversion of ammonia. Biological or biochemical reduction to nitrogen gas can reduce the NO_2 + NO_3 level in natural samples.

NITROGEN-NITRATE+NITRITE Filtered
High Range

QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	1.00	3.00	4.08±1.13	4.08±0.75	2.08±0.58	2.08±0.38	0.13	0.21
1983	1.00	3.00	3.90±0.59	3.90±0.39	2.04±0.29	2.04±0.19	0.07	0.11
1984	1.00	3.00	3.99±0.58	3.99±0.39	2.00±0.37	2.00±0.25	0.08	0.12
1985	1.00	3.00	3.98±0.17	3.98±0.11	2.03±0.14	2.03±0.09	0.04	0.04
1986	1.00	3.00	3.98±0.21	3.98±0.14	1.99±0.15	1.99±0.10	0.04	0.04

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	158	30	11	0.0042	0.0046	0.019	2.3	0.39	0.73	0.01
1983	115	21	8	0.01	0.05	0.04	6.8	4.9	1.6	0.03
1984	151	33	14	0.008	0.017	0.048	5.3	1.5	1.8	0.02
1985	129	15	13	0.0056	0.031	0.021	3.4	2.5	0.68	0.02
1986	127	21	5	0.0056	0.024	0.020	2.4	1.0	0.74	0.02

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	1.32	1.32	100
1983	0.535	0.600	112
	1.93	2.05	106
1984	0.027	0.025	93
	0.34	0.35	103
1985	0.66	0.65	98
1986	0.305	0.286	94
	0.570	0.600	105

SAMPLE TYPE: Rivers & Lakes (Surface Waters).

SAMPLE PRESERVATION: Collect sample in a 125 mL polyethylene bottle; no preservatives are added.

SAMPLE PREPARATION: Low level nitrite analyses are completed on a field filtered (0.45 micron pore size) sample.

ANALYTICAL PROCEDURE: In the automated diazotization colorimetric procedure, an aliquot of sample is mixed with a solution of sulphanilamide under acidic conditions to produce a diazo compound which couples with N-(1-naphthyl)ethylene to form a purple-red azo dye.

INSTRUMENTATION: A Technicon AutoAnalyzer II system with a 50 mm flow cell measures the absorbance at 520 nm. A stripchart recorder displays the sample peaks.

LOW RANGE

ANALYTICAL RANGE: 0.001-0.200 mg/L N LOWEST REPORTED VALUE: <0.001 mg/L N

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 0.001 mg/L N

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A+B)}$ LIMITS		$\overline{(A-B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.150	0.050	0.198±0.008	0.198±0.006	0.099 ±0.004	0.099±0.003

WITHIN-RUN STD DEVIATION: 0.0007 BETWEEN-RUN STD DEVIATION: 0.002

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	31	3	1
STANDARD DEVIATION	0.0003	0.0033	0.0007
PRECISION (% RSD)	7.2	8.7	0.5

DETECTION LIMIT: 0.001 mg/L N

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
	NONE COMPLETED	

COMMENTS: Nitrites readily convert to nitrate by oxidation processes and to nitrogen gas through reduction processes. Samples must be analyzed within hours of sample collection to obtain meaningful data.

NITROGEN-NITRITE, Filtered
Low Range
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	0.060	0.020	0.079 ± 0.006	0.079±0.004	0.039 ±0.003	0.039 ±0.002	0.0007	0.001
1983	0.060	0.020	0.079 ± 0.008	0.079±0.006	0.038 ±0.008	0.038 ±0.005	0.002	0.002
1984	0.060	0.020	0.081 ± 0.008	0.081±0.005	0.039 ±0.004	0.039 ±0.003	0.0007	0.001
1985	0.060	0.020	0.082 ± 0.004	0.082±0.003	0.040 ±0.003	0.040 ±0.002	0.0007	0.001
1986	0.060	0.020	0.081 ± 0.005	0.081±0.004	0.040 ±0.003	0.040 ±0.002	0.0007	0.001

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	LIMIT, mg/L
1982	6	-	-	0.0001	-	-	1.6	-	-	0.0003
1983	92	12	2	0.0002	0.0006	0.002	2.8	2.4	3.6	0.0006
1984	81	6	-	0.0002	0.002	-	3.9	5.4	-	0.0006
1985	77	7	3	0.0003	0.0004	0.0007	4.9	1.6	1.1	0.0009
1986	21	4	1	0.0011	0.0009	0.0007	21.0	3.2	1.3	0.003

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	-	-	-
1983	-	-	-
1984	-	-	-
1985	-	-	-
1986	-	-	-

SAMPLE TYPE: Drinking Waters and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 125 mL polyethylene bottle; no preservatives are added.

SAMPLE PREPARATION: An aliquot of sample is filtered through a 0.45 micron membrane filter at the laboratory. Low level nitrite analyses are completed on a field filtered (0.45 micron pore size) sample.

ANALYTICAL PROCEDURE: In the automated diazotization colorimetric procedure, an aliquot of sample is mixed with a solution of sulphanilamide under acidic conditions to produce a diazo compound which couples with N-(1-naphthyl)ethylene to form a purple-red azo dye.

INSTRUMENTATION: A Technicon AutoAnalyzer II system with a 50 mm flow cell measures the absorbance at 520 nm. A stripchart recorder displays the sample peaks.

HIGH RANGE

ANALYTICAL RANGE: 0.05-1.5 mg/L LOWEST REPORTED VALUE: <0.001 mg/L N

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 0.001 mg/L N

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A+B)}$ LIMITS		$\overline{(A-B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.10	0.401	0.493±0.021	0.493±0.014	0.302±0.016	0.302±0.011

WITHIN-RUN STD DEVIATION: 0.0035 BETWEEN-RUN STD DEVIATION: 0.004

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	70	18	8
STANDARD DEVIATION	0.003	0.003	0.004
PRECISION (% RSD)	30.0	2.0	1.1

DETECTION LIMIT: 0.009 mg/L N

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
	NONE COMPLETED	

COMMENTS: Nitrites readily convert to nitrate by oxidation processes and to nitrogen gas through reduction processes. Samples must be analyzed within hours of sample collection to obtain meaningful data.

NITROGEN-NITRITE, Filtered
High Range
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	1.00	3.00	3.97 ± 0.65	3.97 ±0.44	1.99 ±0.32	1.99 ±0.22	0.078	0.120
1983	1.00	3.00	3.91 ± 0.47	3.91 ±0.31	2.03 ±0.24	2.03 ±0.16	0.056	0.090
1984	1.00	3.00	4.02 ± 1.95	4.02 ±1.30	2.00 ±1.12	2.00 ±0.75	0.026	0.460
1985	1.00	3.00	3.97 ± 0.27	3.97 ±0.18	1.98 ±0.19	1.98 ±0.13	0.041	0.050
1986	1.00	3.00	3.96 ± 0.24	3.96 ±0.16	1.98 ±0.15	1.98 ±0.10	0.035	0.050

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	LIMIT, mg/L
1982	55	7	-	0.005	0.013	-	3.4	0.8	-	0.014
1983	48	3	-	0.008	0.023	-	4.1	1.9	-	0.024
1984	71	14	2	0.006	0.016	0.039	4.5	1.4	1.4	0.018
1985	46	12	-	0.005	0.009	-	2.1	0.84	-	0.015
1986	57	3	1	0.003	0.016	0.0071	4.7	1.7	0.27	0.009

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	-	-	-
1983	-	-	-
1984	-	-	-
1985	-	-	-
1986	-	-	-

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 125 mL polyethylene bottle; no preservatives are added.

SAMPLE PREPARATION: Unfiltered sample is mixed prior to filtering an aliquot through precleaned and preheated to 500°C GFC glass fibre filter paper.

ANALYTICAL PROCEDURE: In the thermal combustion method, particulate nitrogen compounds are oxidized to NO_x at 1030°C in the presence of Co_3O_4 + Ag and Cr_2O_3 catalysts. A cyclohexanone-2,4-dinitrophenyl hydrazone combined nitrogen and carbon standard is used to calibrate the analytical system.

INSTRUMENTATION: A Carlo-Erba Model 1106 CHN Analyzer with a thermal conductivity detector measures the amount of nitrogen present in the particulate fraction. An electronic integrator displays the chromatogram and provides a printout of the analytical results.

ANALYTICAL RANGE: 0.02-100 mg/L N LOWEST REPORTED VALUE: <0.02 mg/L N

CALIBRATION: 1 standard RESULTS REPORTED TO NEAREST: 0.01 mg/L N

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
		N/A			

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	102	-	-
STANDARD DEVIATION	0.51	-	-
PRECISION (% RSD)	14.6	-	-

DETECTION LIMIT: 1.5 mg/L N

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
2.04	2.02	99
4.31	4.24	98
5.56	5.76	104

COMMENTS: This method was implemented in 1983. An aliquot of sample is filtered for particulate nitrogen and particulate carbon (simultaneous analysis) upon receipt at the laboratory. Large floating particles are excluded from the aliquot of sample.

NITROGEN, Particulate
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	-	-	-	-	-	-	-	-
1984	-	-	-	-	-	-	-	-
1985	-	-	-	-	-	-	-	-
1986	-	-	-	-	-	-	-	-

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	-	-	-	-	-	-	-	-	-	-
1983	34	-	-	0.18	-	-	24.8	-	-	0.54
1984	72	-	-	0.10	-	-	16.6	-	-	0.30
1985	58	-	-	0.06	-	-	21.5	-	-	0.18
1986	70	-	-	0.07	-	-	14.3	-	-	0.21

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	-	-	-
1983	5.93	5.74	97
	8.86	8.58	97
	12.54	12.49	100
1984	3.78	3.61	96
	7.93	7.91	100
	11.65	11.40	98
1985	1.90	1.91	100
	5.46	5.33	98
	19.22	19.82	103
1986	2.11	2.12	100
	3.07	3.00	98
	5.46	5.39	99

OIL & GREASE
mg/L Oil & Grease
Partition-Gravimetric (P-G)
NAQUADAT #06521
Partition-Infrared (P-I)
NAQUADAT #06524

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 1000 mL glass bottle with a teflon liner. Field preserve with 5 mL of 50% H_2SO_4 (black dot ampoule).

SAMPLE PREPARATION: The entire acidified sample is extracted with three separate portions of Freon in a separatory funnel.

ANALYTICAL PROCEDURE: Oil and grease constituents refers to those substances extracted from the sample into the Freon solvent and measured by the quantitative process. In the partition-gravimetric method (NAQUADAT # 06521), the Freon extract is evaporated (70°C) to a constant weight of oil + grease residue. In the partition infrared method (NAQUADAT # 06524), the absorbance of the Freon extract is measured at 2930 cm^{-1}.

INSTRUMENTATION: A Mettler AE 163 balance measures the partition-gravimetric O&G. A Nicolet MX-S FTIR measures the partition-infrared O&G.

ANALYTICAL RANGE: P-I 0.05 - 80 mg/L O&G LOWEST REPORTED VALUE: P-I <0.05 mg/L O&G
P-G 1 mg/L O&G P-G < 1 mg/L O&G

CALIBRATION: P-I 5 standards RESULTS REPORTED TO NEAREST: P-I 0.05 mg/L O&G
P-G Certified weights P-G 1 mg/L O&G

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
50.0	1.0	52.8±6.5	52.8±4.3	50.6±5.8	50.6±3.9

WITHIN-RUN STD DEVIATION: 1.3 BETWEEN-RUN STD DEVIATION: 1.5

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
22.6	19.2	85

COMMENTS: Freon also extracts selected organic dyes and elemental sulfur.

OIL & GREASE
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	-	-	-	-	-	-	-	-
1984	-	-	-	-	-	-	-	-
1985	-	-	-	-	-	-	-	-
1986	-	-	-	-	-	-	-	-

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	-	-	-	-	-	-	-	-	-	-
1983	-	-	-	-	-	-	-	-	-	-
1984	-	-	-	-	-	-	-	-	-	-
1985	-	-	-	-	-	-	-	-	-	-
1986	-	-	-	-	-	-	-	-	-	-

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	53.0	50.3	95
	66.7	60.7	91
	133.0	126.0	95
1983	-	-	-
1984	19.8	19.1	96
	29.5	29.7	101
1985	20.0	23.8	119
	34.0	26.0	76
1986	20.0	18.3	92

SAMPLE TYPE: Surface Waters, Municipal, and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 2000 mL glass bottle with a teflon cap liner; cool to 4°C and keep out of direct sunlight.

SAMPLE PREPARATION: Unfiltered sample is homogenized and aerated by mixing prior to withdrawing a representative aliquot for analysis.

ANALYTICAL PROCEDURE: In the standard five day BOD procedure, the dissolved oxygen content of natural samples and diluted samples is measured on day 1 and day 5 after incubation at 20°C. Septic samples are seeded with an appropriate microbiological population.

INSTRUMENTATION: A YSI Dissolved Oxygen Meter and oxygen probe measures the oxygen concentration before and after incubation.

ANALYTICAL RANGE: 1-10,000 mg/L O_2 LOWEST REPORTED VALUE: <1.0 mg/L O_2

CALIBRATION: Winkler Titration RESULTS REPORTED TO NEAREST: 1.0 mg/L O_2

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
-	-	-	-	-	-

WITHIN-RUN STD DEVIATION: - BETWEEN-RUN STD DEVIATION: -

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	-	-	-
STANDARD DEVIATION	-	-	-
PRECISION (% RSD)	-	-	-

DETECTION LIMIT:

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
152	138	91

COMMENTS:

OXYGEN DEMAND, Biochemical
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	-	-	-	-	-	-	-	-
1984	-	-	-	-	-	-	-	-
1985	-	-	-	-	-	-	-	-
1986	-	-	-	-	-	-	-	-

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	LIMIT, mg/L
1982	-	-	-	-	-	-	-	-	-	-
1983	-	-	-	-	-	-	-	-	-	-
1984	-	-	-	-	-	-	-	-	-	-
1985	-	-	-	-	-	-	-	-	-	-
1986	-	-	-	-	-	-	-	-	-	-

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	3.2	3.4	106
	83.9	89.0	106
1983	3.2	3.4	106
	83.9	94.0	112
1984	17.2	16.0	93
	51.5	57.7	112
1985	3.2	2.13	67
1986	3.2	3.1	97
	84.4	77.8	92

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 125 mL polyethylene sample container; field preserve with 2 mL of 5% H_2SO_4 (brown dot ampoule).

SAMPLE PREPARATION: An aliquot of unfiltered sample is mixed with potassium dichromate, sulfuric acid, mercuric sulphate and silver sulphate catalyst and sealed in an ampoule which is heated in an oven for 2 h at 150°C.

ANALYTICAL PROCEDURE: In the semi-automated colorimetric procedure, samples are subjected to a severe, oxidative digestion step which is accomplished in sealed ampoules. The chemical oxidation of constituents in the sample consumes dichromate and produces green trivalent chromium compounds.

INSTRUMENTATION: A Technicon AutoAnalyzer II system with a 50 mm flow cell measures the absorbance of green trivalent chromium at 600 nm. A stripchart recorder displays the sample peaks.

ANALYTICAL RANGE: 5-400 mg/L O_2 LOWEST REPORTED VALUE: <5 mg/L O_2

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 5 mg/L O_2

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
300	100	400 ± 44	400 ± 30	197 ± 44	197 ± 29

WITHIN-RUN STD DEVIATION: 10 BETWEEN-RUN STD DEVIATION: 10

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	57	20	7
STANDARD DEVIATION	1.4	2.2	1.8
PRECISION (% RSD)	6.2	2.1	0.6

DETECTION LIMIT: 4 mg/L O_2

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
10	10.3	100
218	224.0	103

COMMENTS: The 5-400 mg/L range for COD was implemented in 1986. Large floating particles are removed from the test aliquot.

OXYGEN DEMAND, Chemical
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	500	300	798 ± 8.6	798 ± 5.7	197 ± 11.5	197 ± 7.7	2.7	2.4
1983	500	300	797 ± 17.0	797 ± 11.3	198 ± 14.5	198 ± 9.7	3.4	3.7
1984	500	300	794 ± 19.1	794 ± 12.7	200 ± 18.7	200 ± 12.5	4.4	4.5
1985	500	300	806 ± 24.1	806 ± 16.0	198 ± 20.3	198 ± 13.5	1.8	5.2
1986	500	300	804 + 16.2	804 + 10.8	199 + 12.7	199 + 8.5	1.5	3.4

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	11	7	2	0.88	2.33	10.8	6.3	2.0	3.6	2.6
1983	5	1	3	4.99	4.81	4.1	2.4	1.5	0.9	14.9
1984	50	19	15	1.3	1.5	7.3	6.6	1.1	1.5	3.9
1985	60	29	27	1.58	2.26	6.02	5.0	1.6	2.2	4.7
1986	63	35	18	1.77	3.33	5.79	6.6	2.9	2.0	5.3

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
	10.4	11.7	112
1982	192.7	188.8	98
	10.4	10.1	97
1983	192.7	189.1	98
	26.0	25.3	97
1984	52.0	48.9	94
	156.0	152.0	97
	10.0	83.0	83
1985	20.0	18.5	92
	100.0	101.4	101
	10.4	9.9	95
1986	145.0	144.9	100

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; field preservatives are not added.

SAMPLE PREPARATION: An aliquot of unfiltered, supernatant sample is taken for analysis.

ANALYTICAL PROCEDURE: pH and total alkalinity are analyzed on the same aliquot of sample.

INSTRUMENTATION: An automatic potentiometric titrator such as a Fisher Titralyzer or Metrohm Titration System measures the initial pH of the sample and subsequently completes the alkalinity titrations.

ANALYTICAL RANGE: 0 - 14 LOWEST REPORTED VALUE: 0.1 pH units

CALIBRATION: 3 standards RESULTS REPORTED TO NEAREST: 0.1 pH units

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
9.2	4.0	13.2 ± 0.11	13.2 ± 0.07	5.2 ± 0.13	9.2 ±0.08

WITHIN-RUN STD DEVIATION: 0.028 BETWEEN-RUN STD DEVIATION: 0.03

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	3	277	8
STANDARD DEVIATION	0.25	0.06	0.02
PRECISION (% RSD)	4.0	0.8	0.2

ACCURACY CHECKS (1987)

THEORETICAL pH	MEASURED pH	% RECOVERY
6.0	6.3	105
7.9	8.0	101

COMMENTS: Loss of CO_2 and degradation of bicarbonates will result in an increase in apparent sample pH.

pH
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	10.7	11.1	21.7±0.9	21.7±0.6	0.3±0.4	0.3 ±0.3	0.07	0.20
1984	8.3	4.5	12.7±0.2	12.7 ±0.1	3.8 ±0.1	3.8 ±0.09	0.03	0.04
1985	8.3	4.5	12.8±0.3	12.8±0.2	3.8±0.4	3.8±0.3	0.07	0.10
1986	9.2	4.0	13.2 ±0.1	13.2 ±0.1	5.2±0.1	5.2±0.07	0.02	0.02

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)		
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%
1982	2	35	15	0.036	0.078	0.07	0.58	0.99	0.82
1983	25	320	102	0.18	0.31	0.096	2.6	2.1	1.1
1984	2	214	80	0.14	0.07	0.027	2.1	0.89	0.48
1985	6	418	131	0.058	0.039	0.019	0.88	0.50	0.23
1986	-	-	573	-	-	0.040	-	-	0.5

ACCURACY CHECKS

YEAR	THEORETICAL pH	MEASURED pH	% RECOVERY
	7.4	7.6	103
1982	8.6	8.6	100
1983	8.6	8.4	98
	7.4	7.3	99
1984	8.6	8.7	101
1985	8.6	8.7	101
	5.5	5.7	104
1986	7.9	7.9	100

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 1000 mL glass bottle with a teflon cap liner; field preserve with 5 mL of 50% H_2SO_4 (black dot ampoule).

SAMPLE PREPARATION: An unfiltered aliquot of homogenized sample is mixed with H_3PO_4 and flash distilled at 155°C in continuous flow distillation system.

ANALYTICAL PROCEDURE: In the automated distillation, 4-aminoantipyrine colorimetric method, an aliquot of distilled sample is buffered to pH 9.2 and is mixed with 4-aminoantipyrine and ferricyanide to form a red coloured antipyrine dye.

INSTRUMENTATION: A Technicon flash distillation unit and AutoAnalyzer II system with a 50 mm flowcell measures the absorbance of the red antipyrine complex at 505 nm. The peaks are displayed on a stripchart recorder.

ANALYTICAL RANGE: 0.001-0.100 mg/L Phenol LOWEST REPORTED VALUE: <0.001 mg/L P

CALIBRATION: 3 standards RESULTS REPORTED TO NEAREST: 0.001 mg/L P

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.075	0.025	0.099±0.003	0.099±0.002	0.050±0.003	0.050±0.002

WITHIN-RUN STD DEVIATION: 0.0007 BETWEEN-RUN STD DEVIATION: 0.001

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	51	35	26
STANDARD DEVIATION	0.0006	0.0008	0.0016
PRECISION (% RSD)	5.3	2.7	2.4

DETECTION LIMIT: 0.002 mg/L Phenol

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.072	0.070	97
0.072	0.071	99

COMMENTS: Certain para-substituted phenolic compounds do not react with 4-aminoantipryrine. Therefore, analysis represents a minimum concentration of phenolics in the sample.

PHENOLIC COMPOUNDS
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	0.075	0.025	0.101 ±0.007	0.101 ±0.005	0.051±0.004	0.051 ±0.003	0.0007	0.0010
1983	0.075	0.025	0.099 ±0.004	0.099 ±0.003	0.050±0.007	0.050 ±0.004	0.0010	0.0010
1984	0.075	0.025	0.100 ±0.003	0.100 ±0.002	0.049±0.003	0.049 ±0.002	0.0007	0.0010
1985	0.075	0.025	0.099 ±0.005	0.099 ±0.003	0.050±0.005	0.050 ±0.003	0.0014	0.0010
1986	0.075	0.025	0.099 ±0.003	0.099 ±0.002	0.049±0.003	0.049 ±0.002	0.0007	0.0010

DUPLICATE DATA

Year	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	LIMIT, mg/L
1982	25	15	2	4.8×10^{-4}	4.6×10^{-4}	1.1×10^{-3}	5.3	1.7	1.4	0.001
1983	53	25	5	8.9×10^{-4}	1.1×10^{-3}	7.1×10^{-4}	11.3	3.9	1.1	0.002
1984	65	51	14	9.6×10^{-4}	1.5×10^{-3}	1.4×10^{-3}	10.3	4.4	2.0	0.002
1985	42	34	9	1.3×10^{-3}	1.4×10^{-3}	1.3×10^{-3}	9.8	4.6	1.6	0.004
1986	44	32	13	9.2×10^{-4}	1.1×10^{-3}	9.8×10^{-4}	8.0	3.3	1.5	0.002

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
	0.012	0.011	92
1982	0.024	0.024	100
	0.012	0.012	100
1983	0.068	0.069	102
	0.012	0.012	100
1984	0.040	0.038	95
	0.068	0.066	97
	0.032	0.032	100
1985	0.064	0.063	98
	0.068	0.066	97
1986	0.040	0.039	98

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 125 mL polyethylene sample container; keep cool (4°C) and out of direct sunlight. No preservatives are added.

SAMPLE PREPARATION: Field filter sample through 0.45 micron membrane filter.

ANALYTICAL PROCEDURE: In the automated heteropoly blue colorimetric method, an aliquot of sample is mixed with ammonium molybdate and antimonyl tartrate which under acidic conditions produces a yellow phosphomolybdic acid that is reduced to a hetropoly blue complex using ascorbic acid.

INSTRUMENTATION: A Technicon AutoAnalyzer II system with a 50 mm flowcell measures the absorbance at 880 nm. A strip chart recorder displays the sample peaks.

ANALYTICAL RANGE: 0.001-0.100 mg/L P LOWEST REPORTED VALUE: <0.001 mg/L P

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 0.001 mg/L P

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.075	0.025	0.100±0.006	0.100±0.004	0.049±0.007	0.049±0.004

WITHIN-RUN STD DEVIATION: 0.001 BETWEEN-RUN STD DEVIATION: 0.002

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	25	5	4
STANDARD DEVIATION	0.0011	0.0008	0.0012
PRECISION (% RSD)	-	3.0	2.2

DETECTION LIMIT: 0.003 mg/L P

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.50	0.50	100

COMMENTS: Samples should be analyzed within 48 hours upon receipt at the laboratory to minimize conversion of orthophosphates.

PHOSPHORUS, Filtered Reactive
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	0.075	0.025	0.098 ±0.007	0.098 ±0.005	0.050 ±0.007	0.050 ±0.005	0.0014	0.0020
1983	0.075	0.020	0.093 ±0.013	0.093 ±0.009	0.052 ±0.012	0.052 ±0.008	0.0028	0.0030
1984	0.075	0.020	0.095 ±0.007	0.095 ±0.005	0.055 ±0.006	0.055 ±0.004	0.0014	0.0020
1985	0.075	0.025	0.095 ±0.005	0.095 ±0.004	0.055 ±0.005	0.055 ±0.003	0.0014	0.0010
1986	0.075	0.020	0.095 ±0.003	0.095 ±0.002	0.055 ±0.003	0.055 ±0.002	0.0014	0.0010

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	46	29	23	3.9×10^{-4}	2.3×10^{-3}	1.2×10^{-3}	6.4	6.0	2.0	0.001
1983	41	17	12	3.3×10^{-4}	1.6×10^{-3}	2.8×10^{-3}	13.9	5.3	3.5	0.001
1984	119	36	20	6.1×10^{-4}	7×10^{-4}	8.4×10^{-4}	7.2	2.5	1.3	0.002
1985	71	15	35	1.8×10^{-4}	4.2×10^{-4}	6.0×10^{-4}	3.8	1.4	0.8	0.001
1986	26	9	13	4.6×10^{-4}	7.1×10^{-4}	1.36×10^{-3}	8.7	2.4	1.9	0.001

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	0.040	0.037	92
	0.216	0.212	98
	0.270	0.265	98
1983	-	-	-
1984	0.050	0.048	96
	0.054	0.053	98
1985	0.032	0.032	100
	0.040	0.037	92
1986	0.040	0.038	95
	0.270	0.265	98

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 125 mL polyethylene bottle; field preserve with 2 mL of 5% H_2SO_4 (brown dot ampoule).

SAMPLE PREPARATION: Unfiltered sample is mixed prior to withdrawing an aliquot for digestion with H_2SO_4, K_2SO_4 and HgO catalyst. A two stage heating cycle (200°C and 360°C) converts organic and inorganic phosphorus compound to orthophosphate, PO_4.

ANALYTICAL PROCEDURE: In the block digestion automated heteropoly blue method, an aliquot of digested sample is mixed with molybdate and antimonyl tartrate under acidic conditions to produce a phosphomolybdic acid which is reduced to a heteropoly blue complex using ascorbic acid.

INSTRUMENTATION: A Technicon AutoAnalyzer II system with a 50 mm flowcell measures the absorbance at 880 nm. A strip chart recorder displays the sample peaks.

ANALYTICAL RANGE: 0.006-0.200 mg/L P LOWEST REPORTED VALUE: <0.006 mg/L P

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 0.001 mg/L P

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.150	0.050	0.200±0.005	0.200±0.003	0.099±0.004	0.099±0.003

WITHIN-RUN STD DEVIATION: 0.0007 BETWEEN-RUN STD DEVIATION: 0.001

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	61	25	26
STANDARD DEVIATION	0.0011	0.0019	0.0023
PRECISION (% RSD)	7.1	3.0	1.8

DETECTION LIMIT: 0.003 mg/L P

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1.50	1.52	101

COMMENTS: Total phosphorus is simultaneously analyzed from the same sample aliquot for TKN.

PHOSPHORUS, Total
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	0.150	0.050	0.201 ±0.008	0.201 ±0.005	0.101±0.008	0.101 ±0.005	0.002	0.002
1983	0.150	0.050	0.202.±0.009	0.202 ±0.006	0.099±0.008	0.099 ±0.005	0.002	0.002
1984	0.150	0.050	0.202 ±0.006	0.202 ±0.004	0.100±0.004	0.100 ±0.003	0.001	0.001
1985	0.150	0.050	0.201 ±0.004	0.201 ±0.003	0.094±0.106	0.094 ±0.071	0.025	0.018
1986	0.150	0.050	0.203 ±0.006	0.203 ±0.004	0.099±0.006	0.099 ±0.004	0.001	0.001

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	58	69	52	4.0×10^{-4}	8.0×10^{-4}	2.2×10^{-3}	2.9	1.3	1.1	0.001
1983	39	31	24	1.5×10^{-3}	2.4×10^{-3}	3.2×10^{-3}	11.5	3.5	3.1	0.004
1984	143	66	45	1.4×10^{-3}	1.9×10^{-3}	2.0×10^{-3}	9.6	3.4	1.5	0.004
1985	148	47	34	7.2×10^{-4}	1.7×10^{-3}	2.1×10^{-3}	6.5	2.6	1.6	0.002
1986	67	33	36	4.8×10^{-3}	1.9×10^{-3}	3.8×10^{-3}	9.7	2.8	2.6	0.001

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	0.93	0.93	100
	0.140	0.147	105
1983	-	-	-
1984	0.070	0.066	94
	0.140	0.140	100
1985	0.104	0.105	101
	0.112	0.110	98
	0.832	0.85	102
1986	0.050	0.046	92
	0.14	0.140	100
	1.50	1.47	98

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; no preservatives are added.

SAMPLE PREPARATION: An aliquot of sample is filtered through 0.45 micron membrane filter at the laboratory.

ANALYTICAL PROCEDURE: In the automated flame photometry method, an aliquot of filtered sample is mixed with a lithium nitrate internal standard and aspirated directly into an air-natural gas flame.

INSTRUMENTATION: A Technicon Flame IV Photometer measures the light emission at 768 nm. The sample peaks are displayed on a strip chart recorder.

ANALYTICAL RANGE: 0.1-10 mg/L K LOWEST REPORTED VALUE: <0.1 mg/L K

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 0.1 mg/L K

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
7.0	3.0	10.0 ±0.5	10.0 ±0.3	4.0 ±0.3	4.0 ±0.2

WITHIN-RUN STD DEVIATION: 0.07 BETWEEN-RUN STD DEVIATION: 0.1

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	119	78	41
STANDARD DEVIATION	0.05	0.06	0.1
PRECISION (% RSD)	4.5	1.9	1.6

DETECTION LIMIT: 0.2 mg/L K

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
5.0	5.1	102
10.0	9.5	95

COMMENTS: Potassium is simultaneously analyzed with sodium, silica, and chloride.

POTASSIUM, Filtered
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	3.0	7.0	9.8 ±0.7	9.8 ±0.5	4.0 ±0.4	4.0 ±0.3	0.07	0.1
1983	3.0	7.0	9.9 ±0.5	9.9 ±0.3	4.0 ±0.4	4.0 ±0.3	0.07	0.1
1984	3.0	7.0	10.1 ±0.5	10.1 ±0.3	4.1 ±0.3	4.1 ±0.2	0.07	0.1
1985	3.0	7.0	10.4 ±0.6	10.4 ±0.4	4.1 ±0.3	4.1 ±0.2	0.07	0.1
1986	3.0	7.0	9.7 ±0.5	9.7 ±0.3	3.9 ±0.3	3.9 ±0.2	0.07	0.1

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	221	120	85	0.023	0.042	0.086	2.5	1.2	1.3	0.07
1983	164	120	93	0.032	0.068	0.090	3.5	2.4	1.1	0.1
1984	207	130	84	0.023	0.048	0.098	2.5	1.5	1.4	0.07
1985	131	121	69	0.029	0.051	0.089	3.1	1.6	1.3	0.09
1986	201	103	46	0.084	0.10	0.11	8.9	3.3	1.6	0.2

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	1.7	1.6	94
	7.2	6.5	90
	9.8	9.3	95
1983	7.2	7.2	100
1984	7.2	7.2	100
1985	7.2	7.0	97
1986	0.88	0.90	102
	18.2	17.5	96

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; field preserve with 5 mL of 50% HNO_3 (blue dot ampoule).

SAMPLE PREPARATION: An aliquot of unfiltered sample is manually digested with HNO_3 and H_2SO_4 until SO_3 fuming occurs. $HClO_4$ is added and heated until fuming occurs.

ANALYTICAL PROCEDURE: In an automated system, an aliquot of digested sample is mixed with 50% HCl and $NaBH_4$ reagent which reduces inorganic selenium to selenide gas (H_2Se) which is stripped from the solution and passed into a heated (combustion) tube furnace.

INSTRUMENTATION: The absorbance of the ground state selenium is measured at 196.1 nm using an Instrumentation Laboratory Video 22 dual channel atomic absorption spectrophotometer. A strip chart recorder displays the peaks.

ANALYTICAL RANGE: 0.0002-0.0050 mg/L Se LOWEST REPORTED VALUE: <0.0002 mg/L Se

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 0.0002 mg/L Se

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.0040	0.0010	0.0050 ± 0.0018	0.0050 ± 0.0012	0.0028 ± 0.0014	0.0028 ± 0.0009

WITHIN-RUN STD DEVIATION: 0.0003 BETWEEN-RUN STD DEVIATION: 0.0004

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	23	1	1
STANDARD DEVIATION	0.00009	0.00021	0.00014
PRECISION (% RSD)	31.7	12.8	5.2

DETECTION LIMIT: 0.0003 mg/L Se

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.0025	0.00237	95
0.0125	0.0120	96

COMMENTS: Selenium and arsenic are simultaneously analyzed on the same aliquot of digested sample.

SELENIUM, Total
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	0.0075	0.0025	0.0099±0.0010	0.0099±0.0007	0.0049±0.0009	0.0049±0.0006	0.0002	0.0002
1983	0.0075	0.0025	0.0101±0.0019	0.0101±0.0013	0.0052±0.0014	0.0052±0.0009	0.0004	0.0004
1984	0.0075	0.0025	0.0095±0.0022	0.0095±0.0015	0.0049±0.0010	0.0049±0.0007	0.0002	0.0004
1985	0.0075	0.0025	0.0094±0.0035	0.0094±0.0024	0.0050±0.0019	0.0050±0.0012	0.0004	0.0008
1986	0.00375	0.00125	0.00510±0.00126	0.00510±0.00084	0.00251±0.00092	0.00251±0.00061	0.0002	0.0003

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	LIMIT, mg/L
1982	6	35	20	-	-	-	-	-	-	-
1983	43	6	-	9×10^{-5}	9.3×10^{-5}	7.1×10^{-5}	24.6	6.5	2.3	0.0003
1984	11	1	-	1×10^{-4}	7×10^{-4}	-	15.6	2.6	-	0.0003
1985	15	2	1	6×10^{-5}	3.5×10^{-5}	3.5×10^{-4}	16.7	1.8	0.84	0.0002
1986	11	-	-	2×10^{-4}	-	-	26.1	-	-	0.0005

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	0.020	0.021	105
	0.040	0.038	95
	0.0635	0.067	106
1983	0.0015	0.0016	107
	0.0060	0.0058	97
	0.030	0.030	100
1984	0.0015	0.0014	93
1985	0.0011	0.0012	109
1986	0.00063	0.00055	87
	0.0055	0.0053	96

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; no preservatives are added.

SAMPLE PREPARATION: An aliquot of sample is filtered through 0.45 micron membrane filter paper at the laboratory.

ANALYTICAL PROCEDURE: In the automated heteropoly blue colorimetric method, an aliquot of sample is mixed with ammonium molybdate at pH 1.2 to produce molybdosilicic acid. Oxalic acid is added to destroy any interfering phosphate complex. The yellow molybdosilicic acid is reduced to the heteropoly blue complex using ascorbic acid.

INSTRUMENTATION: A Technicon AutoAnalyzer II system with a 15 mm flowcell measures the absorbance of the blue coloured complex at 660 nm. A strip chart recorder displays the peaks.

ANALYTICAL RANGE: 0.50-25 mg/L SiO_2 LOWEST REPORTED VALUE: <0.5 mg/L SiO_2

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 0.1 mg/L SiO_2

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
10.7	21.4	33.0 ±1.5	33.0 ±1.0	10.7 ±0.9	10.7 ± 0.6

WITHIN-RUN STD DEVIATION: 0.2 BETWEEN-RUN STD DEVIATION: 0.3

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	66	132	50
STANDARD DEVIATION	0.08	0.11	0.33
PRECISION (% RSD)	6.9	1.3	1.7

DETECTION LIMIT: 0.2 mg/L SiO_2

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
2.14	2.3	107
5.73	6.0	105

COMMENTS: Silica results have been inadvertently reported under NAQUADAT #14102L since 1975. Silica is simultaneously analyzed with sodium, potassium, and chloride.

SILICA, Filtered Reactive
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	7.5	17.5	24.7 ±1.8	24.7 ±1.2	9.9 ±0.7	9.9 ±0.5	0.14	0.30
1983	7.5	17.5	25.6 ±1.8	25.6 ±1.2	10.5 ±0.9	10.5 ±0.6	0.21	0.30
1984	7.5	17.5	24.4 ±1.4	24.4 ±1.0	10.0 ±0.6	10.0 ±0.4	0.14	0.30
1985	5.0	20.0	25.7 ±1.6	25.7 ±1.0	15.7 ±1.1	15.7 ±0.7	0.28	0.30
1986	5.0	20.0	25.2 ±1.7	25.2 ±1.2	15.1 ±0.9	15.1 ±0.6	0.21	0.30

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	LIMIT, mg/L
1982	116	219	107	0.038	0.052	0.16	2.0	1.1	1.1	0.11
1983	120	224	82	0.042	0.096	0.15	2.2	1.2	0.88	0.12
1984	104	225	79	0.056	0.088	0.11	2.1	1.1	0.68	0.16
1985	114	257	108	0.069	0.14	0.28	4.5	1.6	1.7	0.21
1986	43	143	66	0.099	0.10	0.14	6.0	1.3	0.8	0.29

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	-	-	-
1983	1.10	1.10	100
	14.7	14.2	97
1984	1.31	1.30	99
	1.33	1.30	98
1985	1.15	1.1	96
	2.55	2.3	90
	2.6	2.4	92
1986	2.4	2.3	96
	14.8	14.7	99

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; no preservatives are added.

SAMPLE PREPARATION: An aliquot of sample is filtered through 0.45 micron membrane filter at the laboratory.

ANALYTICAL PROCEDURE: In the automated flame photometry method, an aliquot of filtered sample is mixed with a lithium nitrate internal standard and aspirated directly into an air-natural gas flame.

INSTRUMENTATION: A Technicon Flame IV Photometer measures the light emission at 589 nm. The sample peaks are displayed on a strip chart recorder.

ANALYTICAL RANGE: 1-250mg/L Na LOWEST REPORTED VALUE: <1 mg/L Na

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 1 mg/L Na

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
50	200	252 ± 15.5	252 ± 10.3	151 ± 10.6	151 ± 7.1

WITHIN-RUN STD DEVIATION: 2.5 BETWEEN-RUN STD DEVIATION: 3.1

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	112	27	44
STANDARD DEVIATION	0.5	1.2	3.7
PRECISION (% RSD)	7.0	1.4	1.8

DETECTION LIMIT: 2 mg/L Na

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
20.0	19.0	95
40.0	39.5	99

COMMENTS: The 1-250 mg/L Na analytical range was implemented in 1985. Sodium is simultaneously analyzed with potassium, silica, and chloride.

SODIUM, Filtered
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	75	175	246 ±23	246 ±15	98 ±13	98 ± 9	3	4
1983	75	175	252 ±16	252 ±11	99 ± 6	99 ± 4	1	3
1984	75	175	255 ±18	255 ±12	101 ±13	101 ± 8	3	4
1985	50	200	255 ±15	255 ±10	153 ±12	153 ± 8	3	3
1986	50	200	253 ±11	253 ± 7	151 ± 7	151 ± 5	1	2

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	LIMIT, mg/L
1982	88	57	56	1.1	1.3	2.2	9.2	1.7	1.1	3.4
1983	166	60	176	0.70	1.1	5.9	6.6	1.4	1.5	2.1
1984	181	80	63	0.45	1.0	2.3	4.4	1.2	1.1	1.3
1985	148	57	42	0.51	1.6	2.9	4.7	1.9	1.6	1.5
1986	160	74	37	0.31	1.4	2.3	2.7	1.7	1.3	0.9

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	46.6	46	99
	147	146	99
	1000	968	97
1983	40	42	105
1984	40	42	105
1985	40	40	100
1986	19	21	110
	59.5	61	102

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 2000 mL glass container; cool to 4°C and keep out of direct sunlight.

SAMPLE PREPARATION: Sample is homogenized prior to removing an aliquot for analysis.

ANALYTICAL PROCEDURE: In the gravimetric method, (April 1, 1987 forward), an aliquot (50 mL minimum) of homogenized sample is evaporated at 98°C in a preweighed dish and dried to constant weight at 103 - 105°C in an oven. Prior to March 31, 1987, total solids measurements were completed by difference calculation (Microgravimetric method - NAQUADAT 10474L).

INSTRUMENTATION: Mettler AE 163 single pan balance.

ANALYTICAL RANGE: 10-30,000 mg/L Solids LOWEST REPORTED VALUE: <10 mg/L Solids

CALIBRATION: Internal standard RESULTS REPORTED TO NEAREST: 10 mg/L Solids
Certified weights

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
NONE AVAILABLE					

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	54	-	-
STANDARD DEVIATION	13.2	-	-
PRECISION (% RSD)	2.1	-	-

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
NONE AVAILABLE		

COMMENTS: Method change implemented on April 1, 1987, Microgravimetric method changed to gravimetric method. Reference materials are not available for solids measurements.

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 2 L glass container; cool to 4°C and keep out of direct sunlight.

SAMPLE PREPARATION: Gravimetric method (April 1, 1987 forward) Reeve Angel glass fibre filter papers are rinsed, dried, and pre-weighed. Microgravimetric method (NAQUADAT #10453 - prior to March 31, 1987). Nucleopore 0.4 micron membrane filters were preweighed.

ANALYTICAL PROCEDURE: In the gravimetric method, an aliquot (50 mL minimum) of homogenized sample is filtered through a preweighed 1-2 micron Reeve Angel glass fibre filter which is subsequently oven dried for 1 hour at 103 - 105°C. In the microgravimetric method, a 5 mL aliquot of homogenized sample was filtered through a preweighed 0.4 micron Nucleopore membrane filter which was subsequently dried for 30 minutes at 103 -105°C.

INSTRUMENTATION: Mettler BE 22 Balance Control; Mettler ME 22 Balance Pan and Mettler BA 25 Digital Balance Display.

ANALYTICAL RANGE: 1 - 20,000 mL Solids LOWEST REPORTED VALUE: <1 mg/L Solids

CALIBRATION: Internal standards RESULTS REPORTED TO NEAREST: 1 mg/L Solids
Certified weights

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
NONE AVAILABLE					

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	73	-	1
STANDARD DEVIATION	1.5	-	73.5
PRECISION (% RSD)	8.1	-	0.49

DETECTION LIMIT: 4 mg/L Solids

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
NONE AVAILABLE		

COMMENTS: Reference materials are not available for solids measurements.

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; no preservatives are added.

SAMPLE PREPARATION: Unfiltered sample is mixed prior to introducing an aliquot into the 25°C thermostated conductivity cell.

ANALYTICAL PROCEDURE: Specific conductance is defined as the conductivity (the reciprocal of resistivity) of a conductor 1 cm long and 1 cm^2 in cross-sectional area at a specified temperature and is reported as microsiemens per centimeter (µS/cm).

INSTRUMENTATION: A Radiometer CDM 83 conductivity meter measures the conductivity of the sample in a thermostated (25°C) flowcell. A digital display of the conductivity result is provided.

ANALYTICAL RANGE: 0.4-130,000 µS/cm LOWEST REPORTED VALUE: <0.4 µS/cm

CALIBRATION: A series of 5 standards is available for the complete range.

RESULTS REPORTED TO NEAREST: 0.1 below 10
1 above 10
10 above 1300

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
1272	132	1405±5	1405±3	1138±4	1138±3

WITHIN-RUN STD DEVIATION: 1 BETWEEN-RUN STD DEVIATION: 1

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	292	176	22
STANDARD DEVIATION	1.2	2.6	3.2
PRECISION (% RSD)	0.26	0.15	0.10

ACCURACY CHECKS (1987)

THEORETICAL CONDUCTIVITY, µs/cm	MEASURED CONDUCTIVITY, µs/cm	% RECOVERY
228	234	103
606	605	100
897	901	100

COMMENTS: Conductivity measurements at 25°C were initiated in 1984.

SPECIFIC CONDUCTANCE
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	600	1600	2127 ±181	2127 ±121	976 ±83	976 ±55	20	33
1983	600	1600	2174 ±112	2174 ± 75	1002 ±50	1002 ±34	12	21
1984	148	1413	1558 ± 15	1558 ± 10	1262 ± 18	1262 ±12	4	4
1985	148	1410	1559 ± 5	1559 ± 3	1261 ± 7	1261 ± 5	1	1
1986	148	1410	1558 ± 2	1558 ± 1	1262 ± 2	1262 ± 1	0.6	0.6

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)		
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%
1982	11	38	12	11	12	48	4	1	2
1983	107	288	64	2	8	33	0.8	0.8	1
1984	11	44	6	0.4	1	5	0.3	0.1	0.2
1985	112	352	63	1.06	3	6	0.4	0.3	0.2
1986	92	384	27	0.70	2.2	6.2	0.4	0.2	0.2

ACCURACY CHECKS

YEAR	THEORETICAL CONDUCTIVITY, µs/cm	MEASURED CONDUCTIVITY, µs/cm	% RECOVERY
1982	113	119	105
	125	125	100
	572	593	104
1983	479	510	109
1984	479	479	100
1985	479	484	101
1986	443	456	103
	894	913	102

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; no preservatives are added.

SAMPLE PREPARATION: An aliquot of sample is filtered through 0.45 micron membrane filter at the laboratory.

ANALYTICAL PROCEDURE: In the automated methylthymol blue (MTB) colorimetric method, an aliquot of filtered sample is passed through a cation exchange column to remove interfering ions prior to mixing the sample with MTB reagent. Barium is removed from the Ba-MTB complex through precipitation with sulphate. At pH 10.1, free barium reacts with methylthymol blue to form a blue chelate. Uncomplexed MTB reagent is grey.

INSTRUMENTATION: A Technicon Auto Analyzer II system using a 15 mm flowcell measures the absorbance of the uncomplexed MTB at 460 nm which is directly proportional to the concentration of sulphate in the sample.

ANALYTICAL RANGE: 5-300 mg/L SO_4 LOWEST REPORTED VALUE: <5 mg/L SO_4

CALIBRATION: 6 standards RESULTS REPORTED TO NEAREST: 5 mg/L SO_4

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
100	200	301±10	301 ±7	100 ±8	100 ±6

WITHIN-RUN STD DEVIATION: 2 BETWEEN-RUN STD DEVIATION: 2

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	172	83	38
STANDARD DEVIATION	1.1	1.9	5.0
PRECISION (% RSD)	13.3	1.9	2.3

DETECTION LIMIT: 3 mg/L SO_4

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
20	21	108
40	41	102

COMMENTS: Nonlinear calibration curve reduces the accuracy of sulphate results at low and high end of analytical range.

SULPHATE, Filtered

QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	100	300	407 ±141	407 ±94	215 ±72	215 ±48	17	26
1983	100	300	408 ± 39	408 ±26	201 ±31	201 ±21	7	8
1984	100	300	400 ± 19	400 ±12	204 ±13	204 ± 9	3	4
1985	100	300	399 ± 25	399 ±16	201 ±17	201 ±11	4	5
1986	100	300	402 ± 76	402 ±51	201 ±30	201 ±20	7	20

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	LIMIT, mg/L
1982	253	100	55	2.4	3.2	4.8	10.6	2.4	1.7	7.2
1983	184	80	56	1.6	3.1	4.3	7.3	2.5	1.6	4.8
1984	248	114	48	1.5	2.9	5.7	6.3	2.4	2.0	4.5
1985	188	92	48	1.5	2.5	4.8	6.8	1.9	1.6	4.5
1986	185	77	31	1.4	3.5	4.6	6.1	2.8	1.6	4.2

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
	12	10	83
1982	75	67	89
	71	74	104
1983	75	75	100
	183	186	102
1984	17	16	94
	75	74	99
1985	94	91	97
	71	72	101
1986	37	36	97

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 2000 mL glass bottle with a teflon cap liner; no preservatives are added.

SAMPLE PREPARATION: Unfiltered sample is homogenized before withdrawing an aliquot for analysis.

ANALYTICAL PROCEDURE: In the automated solvent extraction procedure, samples are acidified and LAS substances are complexed with methylene blue which is extracted into chloroform. Anionic surfactants are measured by comparison of the absorbance with a linear alkylbenzene sulfonate, prepared reference standard.

INSTRUMENTATION: A Technicon AutoAnalyzer II system with a 50 mm flow cell measures the absorbance of blue chloroform extract at 650 nm. The peaks are displayed on a stripchart recorder.

ANALYTICAL RANGE: 0.04-2.0 mg/L LAS LOWEST REPORTED VALUE: <0.04 mg/L LAS

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 0.01 mg/L LAS

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WING	CONTROL	WARNING
1.50	0.50	2.00±0.10	2.00±0.07	1.01±0.09	1.01±0.06

WITHIN-RUN STD DEVIATION: 0.02 BETWEEN-RUN STD DEVIATION: 0.02

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	21	32	34
STANDARD DEVIATION	0.01	0.02	0.04
PRECISION (% RSD)	7.5	3.7	2.9

DETECTION LIMIT: 0.03 mg/L LAS

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1.00	1.09	109
1.00	1.06	106

COMMENTS: Foam formation should be avoided prior to removing an aliquot of sample for analysis.

SURFACTANTS (Methylene Blue Active Substances)

QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER						STD. DEVIATION	
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	WITHIN RUN	BETWEEN RUN
1982	1.50	0.50	1.99± 0.11	1.99± 0.07	1.02± 0.06	1.02± 0.04	0.01	0.02
1983	1.50	0.50	2.00± 0.10	2.00± 0.07	1.01± 0.08	1.01± 0.05	0.02	0.02
1984	1.50	0.50	2.02± 0.13	2.02± 0.09	1.00± 0.08	1.00± 0.05	0.02	0.03
1985	1.50	0.50	2.02± 0.10	2.02± 0.06	0.98± 0.10	0.98± 0.07	0.02	0.02
1986	1.50	0.50	2.01± 0.08	2.01± 0.05	1.00± 0.07	1.00± 0.05	0.01	0.02

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	21	21	1	0.01	0.01	0.02	4.2	1.9	1.8	0.03
1983	36	22	4	0.01	0.02	0.02	10.4	3.5	2.1	0.03
1984	30	35	8	0.02	0.02	0.02	7.7	3.6	1.4	0.06
1985	14	39	5	0.02	0.02	0.02	7.3	4.0	1.6	0.06
1986	27	34	7	0.01	0.02	0.04	4.5	2.7	2.5	0.03

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	0.50 5.0	0.48 5.0	96 100
1983	-	-	-
1984	-	-	-
1985	-	-	-
1986	-	-	-

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 1000 mL glass bottle; no preservatives are added.

SAMPLE PREPARATION: Filter an aliquot of sample through 0.45 micron membrane filter prior to analysis.

ANALYTICAL PROCEDURE: An aliquot of filtered sample is mixed with a combination of tungstophosphoric acid and molybdophosphoric acid which are reduced by tannins and lignins (T&L) present in the sample. The resulting blue coloured complex is proportional to the concentration of T&L originally present in the sample.

INSTRUMENTATION: A Shimadzu Bausch & Lomb 210 UV spectrophotometer measures the absorbance of the blue complex at 700 nm using 1 cm quartz cells. A digital display of the absorbance is provided.

ANALYTICAL RANGE: 0.1-6 mg/L TA LOWEST REPORTED VALUE: <0.1 mg/L TA

CALIBRATION: 5 standards RESULTS REPORTED TO NEAREST: 0.1 mg/L TA

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
2.25	0.75	3.20±0.41	3.20±0.27	1.66±0.37	1.66±0.25

WITHIN-RUN STD DEVIATION: 0.08 BETWEEN-RUN STD DEVIATION: 0.09

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	19	8	2
STANDARD DEVIATION	0.017	0.021	0.014
PRECISION (% RSD)	5.7	2.5	0.9

DETECTION LIMIT: 0.05 mg/L TA

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
	NONE AVAILABLE	

COMMENTS: Pure reference standards are not available for this test procedure. All results are expressed in mg/L tannic acid based upon the use of tannic acid standards.

TANNIN AND LIGNINS
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	-	-	-	-	-	-	-	-
1984	-	-	-	-	-	-	-	-
1985	2.5	0.75	3.3 ± 0.45	3.3 ± 0.30	1.8 ± 0.37	1.8 ± 0.25	0.08	0.10
1986	2.5	0.75	3.2 ± 0.15	3.2 ± 0.10	1.7 ± 0.12	1.7 ± 0.08	0.03	0.03

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	-	-	-	-	-	-	-	-	-	-
1983	-	-	-	-	-	-	-	-	-	-
1984	-	-	-	-	-	-	-	-	-	-
1985	27	7	5	0.02	0.041	0.021	8.1	4.6	1.1	0.06
1986	6	5	-	0.059	0.068	-	15.2	8.7	-	0.18

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	2.0	1.9	95
	4.0	4.2	105
	10.0	10.6	106
1983	-	-	-
1984	-	-	-
1985	2.0	2.1	105
	4.5	4.8	107
1986	2.0	1.9	95
	10.0	10.5	105

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; no preservatives are added.

SAMPLE PREPARATION: Unfiltered sample is mixed prior to pouring an aliquot for analysis.

ANALYTICAL PROCEDURE: A beam of visible light is passed through the sample. The amount of light scattered at 90°C is measured and ratioed to the sum of the transmitted and forward scattered light. FORMAZIN standards are utilized to calibrate the system.

INSTRUMENTATION: A Hach Model 18900 Ratio Turbidimeter measures the ratioed scattered light in a 25 mm sample cell. A digital display of the turbidity result is provided. Turbidity results are expressed in Nephelometric Turbidity Units (NTU).

ANALYTICAL RANGE: 0.1-200 NTU LOWEST REPORTED VALUE: <0.1 NTU

CALIBRATION: 2 standards RESULTS REPORTED TO NEAREST: 0.1 NTU below 10
1 NTU above 10

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
NTU	NTU	CONTROL	WARNING	CONTROL	WARNING
NONE AVAILABLE					

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	73	5	-
STANDARD DEVIATION	0.11	0.98	-
PRECISION (% RSD)	4.9	1.9	-

DETECTION LIMIT: 0.3 NTU

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, NTU	NUMBER OF REPLICATE	MEASURED CONCENTRATION, NTU	STANDARD DEVIATION	% RECOVERY
18.0	10	17.9	0.2	99

COMMENTS: Certified reference standards are not available for this test procedure. The presence of large suspended particles and air bubbles cause erratic readings in the low calibration range.

TURBIDITY
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	-	-	-	-	-	-	-	-
1984	-	-	-	-	-	-	-	-
1985	-	-	-	-	-	-	-	-
1986	-	-	-	-	-	-	-	-

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, NTU
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	-	-	-	-	-	-	-	-	-	-
1983	-	-	-	-	-	-	-	-	-	-
1984	-	-	-	-	-	-	-	-	-	-
1985	-	-	-	-	-	-	-	-	-	-
1986	-	-	-	-	-	-	-	-	-	-

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, NTU	NUMBER OF REPLICATE	MEASURED CONCENTRATION, NTU	STANDARD DEVIATION	% RECOVERY
1982	-	-	-	-	-
1983	-	-	-	-	-
1984	-	-	-	-	-
1985	18.0	3	18.2	0.06	101
1985	18.0	12	18.3	0.12	102

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; field preserve with 5 mL of 50% HNO_3 acid (blue dot ampoule).

SAMPLE PREPARATION: A 50 mL aliquot of unfiltered sample is manually digested in a Kjeldahl flask with a mixture of HNO_3 and HCl acids at low heat and evaporated almost to dryness. After cooling, add 10 mL of 10% HCl to dissolve any residue. The sample is transferred to a culture tube for centrifugation to remove suspended materials.

ANALYTICAL PROCEDURE: Automated atomic emission spectrometry by direct aspiration into a high temperature (approximately 6500°K) argon plasma.

INSTRUMENTATION: A JARRELL-ASH (975 PLASMA ATOMCOMP) simultaneous multielement (26 channels) Inductively Coupled Argon Plasma Atomic Emission Spectrometer (ICAP-AES) with PDP-8 microprocessor and Digital Decwriter II printer.

SPECTRAL LINE: 292.4 nm

ANALYTICAL RANGE: 0-0.5 mg/L V LOWEST REPORTED VALUE: <0.001 mg/L V

CALIBRATION: 1 standard RESULTS REPORTED TO NEAREST: 0.001 mg/L V

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A + B)}$ LIMITS		$\overline{(A - B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.400	0.100	0.493±0.028	0.493±0.019	0.298 ±0.026	0.298±0.018

WITHIN-RUN STD DEVIATION: 0.006 BETWEEN-RUN STD DEVIATION: 0.006

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	80	4	-
STANDARD DEVIATION	0.0015	0.0032	-
PRECISION (% RSD)	23.7	2.2	-

DETECTION LIMIT: 0.005 mg/L V

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.125	0.122	98
0.250	0.245	98
0.500	0.480	96

COMMENTS: All ICAP heavy metal parameters, with the exception of boron, are determined simultaneously in a single aliquot of sample.

VANADIUM, Total
QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER							
	A	B	CONTROL LIMITS $\overline{(A+B)}\pm 3s$	WARNING LIMITS $\overline{(A+B)}\pm 2s$	CONTROL LIMITS $\overline{(A-B)}\pm 3s$	WARNING LIMITS $\overline{(A-B)}\pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	0.800	0.020	0.816 ± 0.090	0.816 ± 0.060	0.777 ± 0.087	0.777 ± 0.058	0.020	0.021
1984	0.800	0.020	0.815 ± 0.026	0.815 ± 0.017	0.777 ± 0.025	0.777 ± 0.017	0.006	0.006
1985	0.800	0.020	0.794 ± 0.102	0.794 ± 0.068	0.753 ± 0.099	0.753 ± 0.066	0.023	0.024
1986	0.400	0.100	0.489 ± 0.035	0.489 ± 0.023	0.295 ± 0.032	0.295 ± 0.021	0.008	0.008

DUPLICATE DATA

YEAR	NUMBER			AVERAGE STD. DEV.			PRECISION (% RSD)			DETECTION LIMIT, mg/L
	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	0-20%	20-50%	50-100%	
1982	-	-	-	-	-	-	-	-	-	-
1983	99	2	1	0.0006	0.0045	0.0028	12.9	2.6	0.63	0.002
1984	116	1	3	0.0012	0.0063	0.0068	23.9	6.6	1.5	0.004
1985	126	1	1	0.0011	0.0021	0.021	19.4	1.4	0.92	0.003
1986	28	-	-	0.001	-	-	20.0	-	-	0.003

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	0.060	0.054	90
	0.200	0.190	95
	0.750	0.696	93
1983	0.070	0.064	91
	0.250	0.232	93
	0.850	0.814	96
1984	0.250	0.226	90
	0.850	0.834	98
1985	0.011	0.011	100
	0.170	0.163	96
	0.478	0.457	96
1986	0.423	0.411	97
	0.846	0.807	95
	1.692	1.633	96

SAMPLE TYPE: Drinking Water, Surface Waters, Municipal and Industrial Wastes.

SAMPLE PRESERVATION: Collect sample in a 500 mL polyethylene bottle; field preserve with 5 mL of 50% HNO_3 acid (blue dot ampoule).

SAMPLE PREPARATION: A 50 mL aliquot of unfiltered sample is manually digested in Kjeldahl flasks with a mixture of HNO_3 and HCl acids at low heat and evaporated almost to dryness. After cooling, add 10 mL of 10% HCl to dissolve any residue. The sample is transferred to a culture tube for centrifugation to remove suspended materials.

ANALYTICAL PROCEDURE: Automated atomic emission spectrometry by direct aspiration into a high temperature (approximately 6500°K) argon plasma.

INSTRUMENTATION: A JARRELL-ASH (975 PLASMA ATOMCOMP) simultaneous multielement (26 channels) Inductively Coupled Argon Plasma Atomic Emission Spectrometer (ICAP-AES) with PDP-8 microprocessor and Digital Decwriter II printer.

SPECTRAL LINE: 213.8 nm

ANALYTICAL RANGE: 0-0.5 mg/L Zn LOWEST REPORTED VALUE: <0.001 mg/L Zn

CALIBRATION: 1 standard RESULTS REPORTED TO NEAREST: 0.001 mg/L Zn

QUALITY CONTROL DATA (1987)

A	B	$\overline{(A+B)}$ LIMITS		$\overline{(A-B)}$ LIMITS	
mg/L	mg/L	CONTROL	WARNING	CONTROL	WARNING
0.400	0.100	0.499±0.046	0.499±0.030	0.303 ±0.049	0.303±0.033

WITHIN-RUN STD DEVIATION: 0.011 BETWEEN-RUN STD DEVIATION: 0.011

DUPLICATE DATA (1987)

RANGE	0 - 20%	20 - 50%	50-100%
DUPLICATE SETS (N)	81	12	3
STANDARD DEVIATION	0.0014	0.0035	0.0141
PRECISION (% RSD)	14.2	2.2	3.9

DETECTION LIMIT: 0.004 mg/L Zn

ACCURACY CHECKS (1987)

THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
0.05	0.054	108
0.10	0.107	107
0.20	0.193	97

COMMENTS: All ICAP heavy metal parameters, with the exception of boron, are determined simultaneously in a single aliquot of sample.

ZINC, Total

QUALITY CONTROL DATA

YEAR	CONTROL PARAMETER A	B	CONTROL LIMITS $\overline{(A+B)} \pm 3s$	WARNING LIMITS $\overline{(A+B)} \pm 2s$	CONTROL LIMITS $\overline{(A-B)} \pm 3s$	WARNING LIMITS $\overline{(A-B)} \pm 2s$	STD. DEVIATION WITHIN RUN	STD. DEVIATION BETWEEN RUN
1982	-	-	-	-	-	-	-	-
1983	0.800	0.020	0.822 ± 0.102	0.822 ± 0.068	0.784 ± 0.101	0.784 ± 0.067	0.024	0.024
1984	0.800	0.020	0.821 ± 0.031	0.821 ± 0.021	0.785 ± 0.030	0.785 ± 0.020	0.007	0.007
1985	0.800	0.020	0.832 ± 0.064	0.832 ± 0.043	0.792 ± 0.057	0.792 ± 0.038	0.013	0.014
1986	0.400	0.100	0.492 ± 0.142	0.492 ± 0.095	0.292 ± 0.138	0.292 ± 0.092	0.032	0.033

DUPLICATE DATA

YEAR	NUMBER 0-20%	NUMBER 20-50%	NUMBER 50-100%	AVERAGE STD. DEV. 0-20%	AVERAGE STD. DEV. 20-50%	AVERAGE STD. DEV. 50-100%	PRECISION (% RSD) 0-20%	PRECISION (% RSD) 20-50%	PRECISION (% RSD) 50-100%	DETECTION LIMIT, mg/L
1982	-	-	-	-	-	-	-	-	-	-
1983	116	15	4	0.0036	0.0036	0.026	21.1	2.6	6.2	0.010
1984	130	12	6	0.0019	0.006	0.009	15.6	4.3	2.6	0.006
1985	102	17	9	0.004	0.019	0.0077	19.0	7.2	2.0	0.012
1986	71	7	4	0.003	0.010	0.014	14.8	5.5	4.7	0.009

ACCURACY CHECKS

YEAR	THEORETICAL CONCENTRATION, mg/L	MEASURED CONCENTRATION, mg/L	% RECOVERY
1982	0.200	0.198	99
	0.272	0.279	102
1983	0.080	0.079	99
	0.400	0.390	98
1984	0.080	0.078	98
	0.400	0.408	102
1985	0.014	0.014	100
	0.055	0.055	100
	0.078	0.080	102
1986	0.209	0.204	97
	0.418	0.397	95
	0.836	0.814	97

DISCUSSION

Discussion

The quality control data presented in this report is an evaluation of the overall performance of all analytical systems employed in the Water Analysis Laboratory since 1982. Three basic types of quality control information are produced in this program; (A $\pm$ B) control and warning limits, duplicate data, and recovery data.

First, the control and warning limits established from QCA and QCB data were used to detect the two common types of statistical errors, systematic and random errors. Any individual (A + B) point falling outside the control limits indicated a significant systematic error in calibration which directly affects the accuracy of all analytical results. An out-of-control situation in (A - B) could be a result of gross random error in either A or B. The general rule for selecting the concentration of A and B was based on the assumption that linearity exists over the normal operating range. This implied approximately equal standard deviations for A and B. The irreproducibility of calibration graphs for non-linear systems would therefore affect the analytical precision and consequently the accuracy. Among all the chemical parameters routinely analyzed in the laboratory, sodium, chloride, sulfate, arsenic, selenium, and silica show significant curvature in the calibration curves, usually at high analyte concentration. Table 1 summarizes the useful analytical range commonly used and the linear range above which deviation from linearity occurs.

Table 1. Useful Linear Range for Non-Linear Analytical Systems

Parameter	Analytical Range	QCA	QCB	Linear Range
Na	0-250	187	62	0-170
Cl	1-100	75	25	1-50
SO_4	0-300	225	75	30-200
As	0-0.005	0.004	0.001	0.0005-0.003
Se	0-0.005	0.004	0.001	0.0005-0.004
SiO_2	0.5-25	19	6	5-20

Therefore, narrowing the analytical range would remarkably improve the accuracy of measurements with these systems. However, sample dilution will be required for sample concentrations exceeding the linear segment of the analytical range and errors associated with sample preparation will be introduced.

Second, the overall precision of the different methodologies was evaluated from duplicate data produced over each year period. Precision values in the ranges of 0-20%, 20-50%, and 50-100% of full scale of analytical range define three important types of analytical noise associated with each analytical system. In the 0-20% range the system is background noise-limited and precision improvement in this region will be possible by reducing the background noise. Examples include the use of high purity reagents, minimizing dark current noise by regularly checking the hollow-cathode lamps and photomultiplier tubes, and enhancing the analytical signal by developing alternative methodologies (e.g. preconcentration techniques) that would provide lower detection limits. Concentrations in the 20-50% range show a significant improvement in precision and the system tends to be either shot noise limited or a combination of shot noise and flicker noise. Signal enhancement in this region will be feasible by simultaneously optimizing all experimental variables to attain a maximum instrument response. This will enhance the analytical sensitivity and provide higher signal-to-noise (S/N) ratios. In the region of 50-100% of full scale the system tends to be flicker noise limited and the signal-to-noise ratio is independent of concentration. A constant precision value results and improvement will be practically impossible except by improvement in analytical techniques and skills of the analyst. A more elaborate discussion of S/N ratio is beyond the scope of this report because of the ratio's complexity and its dependence on the methodology as well as the type of instrumentation used. However, the reader is encouraged to refer to a series of articles published by J. Ingle (4) that thoroughly describes the different types of noise associated with spectrochemical analytical instrumentation and methods to improve the overall analytical performance of such systems. Table 2 compares precision data obtained throughout the analytical range from duplicate analyses in 1987. Within-run and between-run standard deviations were calculated from QCA and QCB data.

Table 2. Comparison Between Precision Data Obtained from Duplicate Analysis with Within-Run and Between-Run Standard Deviation Calculated from QCA and QCB Data.

Parameter	Precision, % RSD (Duplicate Data)			Standard Deviation (QCA and QCB Data)	
	0-20%	20-50%	50-100%	Within-Run	Between-Run
Al	10.2	5.6	4.6	0.020	0.024
Alkalinity	0.6	0.2	0.2	2.8	3.6
As	28.6	14.0	16.0	0.0002	0.0002
B	11.9	1.5	1.0	0.005	0.009
Ba	4.8	6.8	4.3	0.007	0.008
Be	33.1	1.3	-	0.007	0.007
CN	8.3	5.6	1.8	0.001	0.001
COD	6.2	2.1	0.6	10	10
Ca	15.1	2.3	2.1	2	2
Cd	23.5	2.8	-	0.007	0.008
Cl	12.2	1.7	0.9	1.0	1.0
Co	14.4	0.14	3.8	0.006	0.007
Cr	23.5	1.6	-	0.014	0.014
Cu	14.5	1.7	4.7	0.011	0.011
DIC	14.7	1.4	1.0	0.5	0.9
DOC	18.6	2.4	1.9	0.2	0.3
F	3.7	1.4	1.6	0.02	0.02
Fe	18.3	2.1	0.8	0.01	0.02
Hg	30.0	13.0	3.6	0.00006	0.00007
K	4.5	1.9	1.6	0.07	0.1
MBAS	7.5	3.7	2.9	0.02	0.02
Mg	19.2	2.4	1.4	0.7	1.0
Mn	13.0	4.1	2.6	0.004	0.006
Mo	24.0	4.6	-	0.010	0.010

Table 2. Cont'd.

Parameter	Precision, % RSD (Duplicate Data)			Standard Deviation (QCA and QCB Data)	
	0-20%	20-50%	50-100%	Within-Run	Between-Run
$N\text{-}NH_3$(High)	12.0	2.2	1.6	0.02	0.02
$N\text{-}NH_3$(Low)	13.8	6.7	2.1	0.0035	0.004
$N\text{-}NO_2$(High)	30.0	2.0	1.1	0.0035	0.004
$N\text{-}NO_2$(Low)	7.2	8.7	0.5	0.0007	0.002
$N\text{-}NO_3+NO_2$(High)	9.9	0.8	0.5	0.007	0.010
$N\text{-}NO_3+NO_2$(Low)	23.6	10.8	2.0	0.001	0.001
Na	7.0	1.4	1.8	2.5	3.1
Ni	27.4	2.2	0.3	0.006	0.007
O&G	-	-	-	1.3	1.5
P, Filtered Reactive	-	3.0	2.2	0.001	0.002
P, Total	7.1	3.0	1.8	0.0007	0.001
Pb	16.8	2.0	1.9	0.004	0.006
pH	4.0	0.8	0.2	0.028	0.03
Phenols	5.3	2.7	2.4	0.0007	0.001
SO_4	13.3	1.9	2.3	2	2
Se	31.7	12.8	5.2	0.0003	0.0004
SiO_2	6.9	1.3	1.7	0.2	0.3
Specific Conductance	0.26	0.15	0.10	1	1
T&L	5.7	2.5	0.9	0.08	0.09
TKN	13.0	3.9	2.4	0.016	0.019
TSS	8.1	-	0.49	-	-
Turbidity	4.1	1.9	-	-	-
V	23.7	2.2	-	0.006	0.006
Zn	14.2	2.2	3.9	0.011	0.011

The detection limits reported from duplicate data, in the 0-20% range of full scale, were calculated by multiplying the standard deviation within the 0-20% range by 3. This is compatible with the definition of detection limit "Signal-to-Noise Ratio = 3" (3). Analysts who develop new or modified instrumentation for trace analysis often define detection limits in terms of the standard deviation of measurements of the blank. However, the blank referred to is not a field blank containing sample matrix, but simply the solvent in which the sample is presented to the instrument. This convention is a rapid way of comparing instruments or assessing the effects of any changes made in the course of development. However, in relation to practical analysis, these "instrumental detection limits" (IDL) are unrealistically low. They have been widely criticized because they cannot be matched in practical circumstances and are therefore misleading to the unwary user of the data. The reasons that IDL values are low include: (i) they do not include the additional variance associated with reagent blank subtraction; (ii) the solution used is matrix free; (iii) the blank solution is not a field blank, i.e., it has not been subjected to all of the many procedures that a real sample solution would experience in the course of an analysis; (iv) the measurements for IDL estimation are made within the shortest time scale, a circumstance that minimizes the variance due to the ubiquitous base-line drift. In practical analysis, the drift occurring between calibration updates would be included in the estimate of the blank standard deviation. Therefore, the use of duplicate data to estimate the detection limit reflects a representative value of the methodology used. Table 3 compares the instrumental detection limits obtained from the blank standard deviation of ten replicate determinations with those obtained from duplicate data produced in 1987.

Table 3. Comparison of Detection Limits Using Duplicate Data Method with the Instrumental Detection Limits (1987).

Parameter	Detection Limit, mg/L	
	Duplicate Data Method	Aqueous Standards Method (IDL)
Al	0.026	0.005
Alkalinity	2.1	1.8
As	0.0003	0.00007
B	0.013	0.004
Ba	0.005	0.001
Be	0.0012	0.0001
CN (Simple)	0.002	0.0005
COD	4	2
Ca	1.8	1.5
Cd	0.0021	0.001
Cl	0.6	0.3
Co	0.006	0.001
Cr	0.004	0.001
Cu	0.004	0.001
DIC	1	0.9
DOC	0.3	0.2
F	0.02	0.006
Fe	0.024	0.028
Hg	0.00012	0.00002
K	0.2	0.05
MBAS	0.03	0.03
Mg	1.2	0.9
Mn	0.004	0.002
Mo	0.004	0.002
$N-NH_3$ (High)	0.015	0.002
$N-NH_3$ (Low)	0.006	0.001
$N-NO_2$ (High)	0.009	0.001

Table 3. Cont'd.

Parameter	Detection Limit, mg/L	
	Duplicate Data Method	Aqueous Standards Method (IDL)
$N-NO_2$ (Low)	0.0009	0.0004
$N-NO_3+NO_2$(High)	0.006	0.009
$N-NO_3+NO_2$(Low)	0.0033	0.0007
Na	1.5	0.2
Ni	0.005	0.002
PO_4	0.003	0.0004
Pb	0.003	0.002
Phenols	0.002	0.0008
SO_4	3.3	1.2
Se	0.0003	0.0001
SiO_2	0.2	0.02
T&L	0.051	N/A
TKN	0.054	0.006
TP	0.003	0.0006
TSS	6	N/A
V	0.004	0.008
Zn	0.004	0.002

It is evident from Table 3 that the IDL for most parameters are lower than the detection limits calculated from duplicate data. This is attributed to the absence of interferences in the blank solutions utilized to determine the IDL. Therefore, it is most significant and practical to use the detection limits derived from duplicate data to include all variances associated in all steps a real sample solution would be subjected to during the course of an analysis.

Finally, the recovery data provided in this report measure the degree of accuracy of the methodology currently used in the laboratory. For the majority of parameters analyzed, the recovery data were very good. However, a more accurate approach to measure recovery in complex matrices would be to spike samples with known amounts of the particular constituent. Accuracy would therefore be reported as the percent recovery at the final concentration of the spiked sample. This method will therefore take into account the additional variance associated with the sample matrix and presents a more realistic assessment of accuracy. Unfortunately this method of standard additions would require significant reductions in the analysis capability of the laboratory. The accuracy of the analytical results routinely produced by the Water Analysis Laboratory has proven to be acceptable to our clients.

RECOMMENDATIONS

The absence of QC data for some analytical parameters in this report will be considered in the 1988 QA/QC Performance Report. The following is a brief description of QC procedures:

Parameter	QCA and QCB	Duplicate
TS	Two Levels of NaCl Solutions	Existed
TSS	Two filter papers of different weights	Existed
BOD	Two different concentrations of Glucose - Glutamic acid	Exist (1988)
O&G	Exist (1988)	Three standards in the ranges 0-20%, 20-50% and 50-100% of full scale
Turbidity	Two concentration levels of Formazin standard	Exist (1988)
PC, PN	Two concentration levels prepared from a composite sample	Existed

REFERENCES

1. W. J. Youden, E. H. Steiner, Statistician Manual of the Association of Official Analytical Chemists, 1975, pp. 1-88.
2. Donald E. King. Quality Control and Data Evaluation Procedures. Ontario Ministry of the Environment Laboratory Services Branch.
3. Analytical Methods Committee. Royal Society of Chemistry, Burlington House, Piccadilly, London WIV OBN, UK. Analyst 1987, Vol. 112, 199.
4. J. D. Winefordner. Advances in Analytical Chemistry Instrumentation, Spectrochemical Methods of Analysis, By John Wiley & Sons, Inc., Vol. 9, 1971, pp. 493-518.

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